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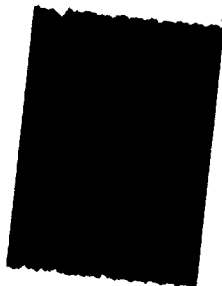
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SYNTHESIS OF MONOMERIC MATERIALS

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MONOMER-POLYMER, INC.

DECEMBER 1954

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WRIGHT AIR DEVELOPMENT CENTER

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DECEMBER 1954

MATERIALS LABORATORY

CONTRACT No. AF 33(616)-252

PROJECT No. 7340

TASK No. 73404

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by the research staff of Monomer-Polymer, Inc. under Contract No. AF33(616)-252. The contract was initiated under Project No. 7340, Rubber, Plastic, and Composite Materials, Task No. 73404, Synthesis and Evaluation of New Polymers, formerly RDO No. 617-11, and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. F. W. Knobloch acting as project engineer. The period covered by this contract was 9 July 1952 to 9 January 1954.

ABSTRACT

In the course of this project, the possibility of preparing the following materials was investigated:

Vinylsilanes
Allyl Sulfides
Divinyl Sulfide
2-Methylthioethyl Vinyl Sulfide
Vinylidene Cyanide
N-(2,2,2-Trifluoroethyl)-acrylamide
N-Alkyl-N-1,1-Dihydroheptafluorobutylacrylamides
N-Alkyl-N-1, 1-Dihydroheptafluorobutylmethacrylamides
Methylene Silanes
1,1-Dihydroheptafluoro-1-butyl alpha-(Trifluoromethyl)-acrylate
1,3-Dicyano-1,3-butadiene
Heptafluoropropylacrylamide

Prior to the attempted preparation of monomers, a comprehensive literative survey was undertaken.

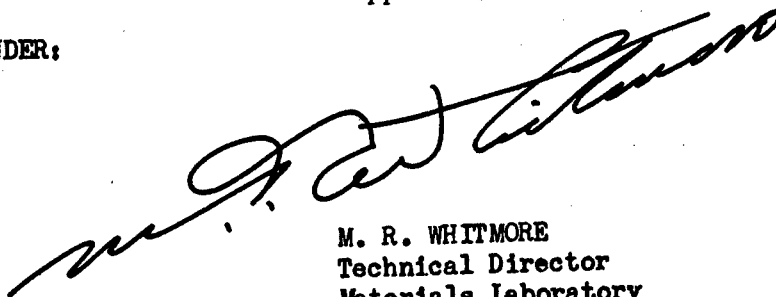
The modification of Acrylon rubbers was investigated by use of both copolymer and terpolymer systems. A preliminary evaluation of the more promising materials was performed.

Samples of monomers and intermediates have been submitted to the Wright Air Development Center.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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INTRODUCTION

It was the purpose of this study, to "investigate the preparation of representative members of certain hypothetical classes of monomeric materials, and, if synthesis proves feasible, to prepare these monomers in such quantities as may be requested" (1).

Investigations into the preparation of new monomeric materials has become a project of major emphasis to the Air Forces synthetic elastomer program. The inability of conventional rubbers to approach satisfactory performance in specialized applications of high temperature and fuel and oil resistance have made it imperative that a program be initiated to explore the preparation of new monomers which may possibly be utilized in tomorrow's rubber formulation.

During the life of this contract, the scope of this project expanded to include not only the preparation but also the polymerization of some of these new monomeric materials.

Copolymerization studies were made, using a large variety of monomers available from the stock of this Laboratory.

This report summarizes the work carried out under the terms of this contract. Although the research carried on between November 9, 1953 and January 9, 1954 has not been reported upon in a bimonthly progress report, this work is incorporated in the body of this final report in detail comparable to that found in the usual bimonthly progress reports.

DISCUSSION

I. Literature Survey

The feasibility of preparing many of the proposed monomers was studied in our extensive literature survey. Methods for the preparation of vinyl silanes, various nitrogen-containing monomers, vinyl sulfides, dithio acrylates, vinyl dithiocarboxylates, fluoroalkylacrylamides, etc., were discussed.

Throughout the period of this contract, the literature was surveyed for specific projects as the need arose. The results of this constantly expanding body of knowledge was generally summarized in the sections headed "Discussion" in the bimonthly progress reports.

The original survey of the literature, it will be noted, did not necessarily cover syntheses of monomers that were actually prepared. This had been anticipated, however, since one of the prime objects of such a survey was to determine the feasibility of preparing new and novel classes of monomers. Those monomers, originally proposed for study, which, as a result of the literature survey appeared impossible or too cumbersome to synthesize were not further investigated.

A. Silicon Containing Monomers:

Very few vinylsilanes of the type --Si--CH=CH_2 have been prepared. Triethylvinylsilane was prepared by Ushakov and Itenberg (2) by partially chlorinating tetraethylsilane and then dehydrohalogenating. Trichlorosilylstyrene has been prepared (3) by dehydrohalogenation of p-trichlorosilyl-2-chloroethylbenzene. A British patent (4) discusses the preparation of divinylchlorosilane by reacting vinyl chloride with copper-silicon alloy at 300° C. Trialkyl- α -chlorovinylsilane is described in a patent (5). Linde Air Products Co. now has trichlorovinylsilane in commercial production. They indicate that many substituted vinyl silanes can be prepared by reacting this silane with various Grignard reagents.

The general method for preparing substituted silanes is to react chlorosilanes with Grignard reagents.

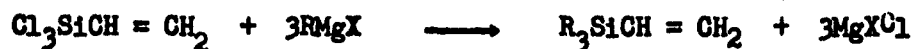


When R is aliphatic, the reaction is nearly quantitative. However, when R is aromatic the Grignard reaction is ineffective. A more efficient

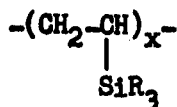
reagent is the aryl lithium derivative.

Kipping and Lloyd (6) have tried to prepare tetraphenylsilane by reacting phenyl magnesium bromide with silicon tetrachloride. They obtained only a triphenylsilane. No evidence of tetrasubstitution was observed. Nevertheless, Gilman and coworkers (7,8,9,10) in a series of papers describe the preparation of tetra-substituted aryl silanes by using aryl lithium derivatives in place of Grignard reagents.

From these data, it is evident that alkyl- and arylvinylsilanes may be made by reacting an alkyl magnesium halide or an aryl lithium with trichlorovinylsilane. Thus, if R is alkyl and R' is aryl, the general equations for the preparation are as shown in the following:

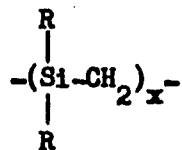


The polymerization of vinylsilanes would proceed through the vinyl group and produce a polymer containing a hydrocarbon chain with pendant tri-substituted silyl groups.



The polymers of this general type would have properties similar to the parent hydrocarbon chain with modification due to the pendant silyl groups. It is conceivably possible that the relative stability of the polymer to various solvents and oxidation conditions would not necessarily be improved by pendant silyl groups since the main skeleton of the polymer remains hydrocarbon in nature.

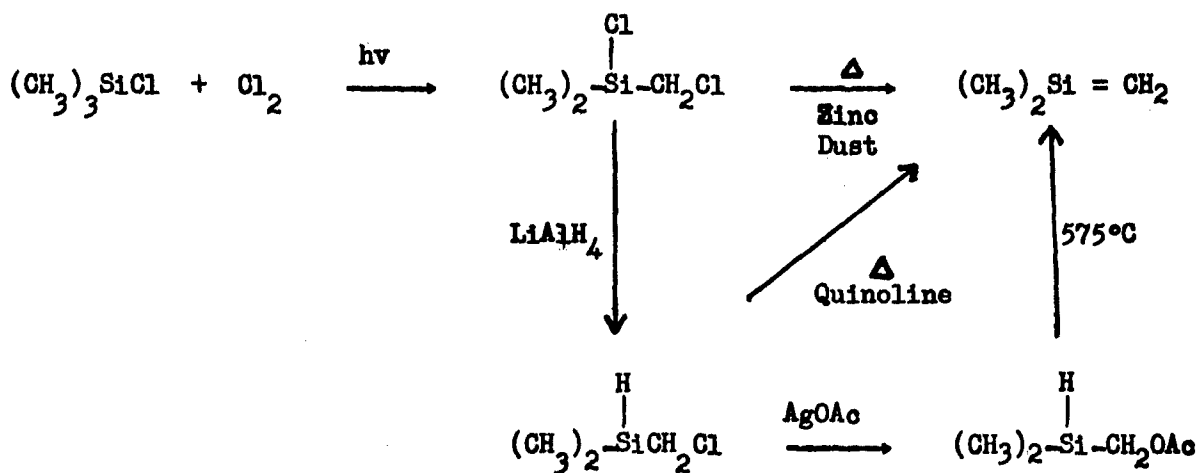
However, if it be possible to prepare a polymer that would contain a carbon-silicon skeleton, then a polymer with marked differences in properties might result. This structure would be:



Attempts to prepare structures, where the value of x is very large have not as yet been accomplished. Sommers, et al. (11) prepared octamethyltrisilylmethylene (where x had a value of 3) by alternate chlorination of tetramethylsilane followed by Grignard treatment. The path to even higher members of the series is outlined by the preparation by Sommers, et al. of pentamethylchloromethylidisilylmethylene. A structure similar to the one above but where a phenylene radical ($-\text{C}_6\text{H}_4-$) replaces the methylene radical has been prepared (12) by reacting p-phenylene di(magnesium bromide) with silicon tetrachloride. The resulting polymers are of very low molecular weight and are sticky, oily resins. Both the above methods are stepwise reactions and the synthesis of a long chain is not readily possible.

Another approach to this problem has been suggested by Rochow (13). His method would utilize the reaction of methylene chloride with silicon-copper alloy to produce a polymethylenedichlorosilane. Reaction of the chloro groups with Grignard reagents would produce the completely substituted polymethylenesilane. Since these reactions are mainly carried out in the vapor phase, it is almost inconceivable that a polymer of long chain length could be produced by this method.

A new approach to this problem is the preparation of compounds with the $\text{R}_2\text{Si} = \text{CH}_2$ structure, which may be considered somewhat similar to $\text{R}_2\text{C} = \text{CH}_2$. If the silicon atom, in this instance, behaves like a carbon atom, then polymerization either by free radical or ionic means should produce a polymer as shown above. From the theoretical standpoint, the synthesis of the monomers would probably be as follows:



B. Nitrogen Containing Monomers.

The polymerizable materials that contain nitrogen and were of interest to this investigation were vinylamines, vinylimides, vinylamides, and vinylidene cyanide.

1. Vinylamines and Methyleneamines:

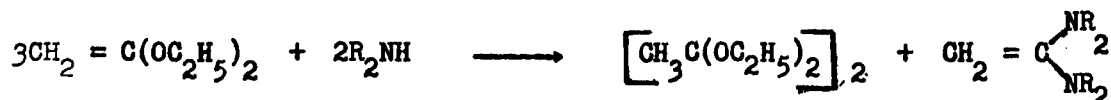
Very few vinylamines of the type $\begin{array}{c} \text{R} \\ \diagdown \\ \text{N}-\text{CH}=\text{CH}_2 \\ \diagup \\ \text{R} \end{array}$ have been prepared.

Vinyldimethylamine and vinyldiethylamine have been prepared in rather low yield by a Hofmann exhaustive methylation procedure (14). Vinylmethylaniline has also been prepared by a method similar to the above (15).

These vinylamines are very unstable and decompose readily to acetaldehyde and the corresponding amine. These products then recombine to form acetaldehyde-amine type condensation polymers.

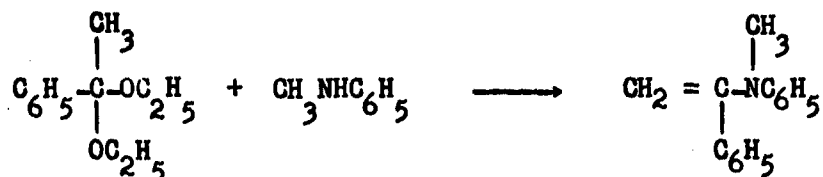
A vinyl group on a nitrogen that is relatively acidic is quite stable. Vinyldiphenylamine is known and is stable. A patent describes its preparation (16). Vincylcarbazole is another example of a stable vinylamine containing acidic nitrogen.

Another type of vinylamine has been described by McElvain and Tate (17). This is 1,1-bis-(dialkylamino)-ethylene, which is made from ketene acetal.



These vinylamines are relatively stable and are prepared in fair yield.

Analogous to this reaction is the one by Hoch (18) which used alkyl ketals.



These compounds are similar in structure to alpha-substituted styrenes. Methyleneamines comprise that group of compounds known as Schiff's - Bases. These are quite stable in the aromatic series, but are difficult to prepare in the aliphatic series. A Schiff's Base that can be prepared and isolated is so stable that it is very unlikely that polymerization of these materials would be possible.

2. Vinylimides:

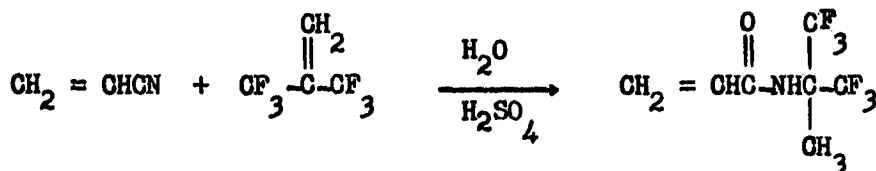
A U. S. patent (19) is the only reference to the preparation of a vinylimide. In this patent, N-vinyl-phthalimide is prepared by the de-acetylation of N-acetoxyethylphthalimide. Mention is made that this imide could also be prepared by the dehydration of N-hydroxyethylphthalimide.

The vinylimides that were of a particular interest to this research work were N-dichlorovinylphthalimide and 1-phthalimidobutadiene.

3. Vinylamides:

The compound that was of interest in this group is a N,N-di-(polyfluorinated alkyl) acrylamide. There are various methods for the preparation of substituted acrylamides. These are the dehydration of alpha- or beta-hydroxypropionamides (20,21), reaction of acrylonitrile with olefins in the presence of concentrated sulfuric acid (22), reaction of acrylyl chloride with amines and dehydrohalogenation of alpha- or beta- chloropropionamides.

Isobutylene reacts with acrylonitrile (22) to give N-tert-butylacrylamide. If fluorinated isobutylene could be used then it is conceivably possible to get N-tert-fluorobutylacrylamide.



The best and most direct method is the reaction of acrylyl chloride with amines. However, amines with perfluorinated alkyl groups are somewhat acidic and it was found that although acrylamides of this type could be made by this method, yields were low.

4. Vinylidene Cyanide:

Vinylidene cyanide or alpha-cyanoacrylonitrile has been prepared (23) by the interaction of formaldehyde on malononitrile. The yields are rather good. The product is water sensitive, giving polyvinylidene cyanide on such treatment.

From theoretical considerations it was anticipated that this material, used in place of acrylonitrile in acrylate-acrylonitrile rubbers, might give a superior fuel and oil resistant rubber.

C. Sulfur Containing Monomers

Three classes of sulfur compounds were to be considered: vinyl sulfides, vinyl esters of dithiocarboxylic acids, and esters of dithioacrylic acid.

1. Vinyl Sulfides:

Although a large number of organic sulfides is known and described in the literature, very few vinyl sulfides have been synthesized. The list includes methyl vinyl sulfide (24), n-butyl vinyl sulfide (25), divinylsulfide (26, 27), and phenyl vinyl sulfide (28, 29). These have all been made by dehydrohalogenating the corresponding chloroethyl derivatives.

Price and Zomlefer (30) have studied the polymerization characteristics of methyl vinyl sulfide. It polymerized quite well with methyl methacrylate, and styrene.

An interesting monomer for oil resistant elastomers would be $R-SCH_2CH_2SCH_2CH_2SCH=CH_2$. The starting material is easily prepared (31).

2. Dithioacrylates and Vinyl Dithiocarboxylates:

This group has not been prepared. No reference could be found to its preparation. Dithioacids are in themselves hardly known. The best method for their preparation is to react a Grignard with carbon disulfide (31, 32). The yields are extremely low, usually in the neighborhood of 3-10%.

It is very possible that, if the dithioacids could be made in fair yield, then vinylation studies could be conducted. However, little hope is held for this particular group of compounds.

D. Fluorine containing Monomers.

Besides the fluoroalkylamines discussed above, the following fluorine containing compounds were considered: pentafluorostyrene and tetrafluoroterephthalic acid.

Direct substitution of the hydrogens on an aromatic nucleus for a fluorine has not been accomplished. Usually, addition to the double bonds occurs first followed by substitution to give the corresponding perfluoroalicyclic compound. The only practical way that a fluorine can be introduced into an aromatic ring is through replacement of a diazonium compound. This is the Schiemann type reaction (33). In this reaction, only one hydrogen is replaced at a time. Finger and Reed in a series of papers (34,35,36,37) have prepared various polyfluorinated benzenes and mesitylene by using this reaction.

When one considers the available starting materials for the preparation of the tetrafluoroterephthalic acid and pentafluorostyrene it becomes clear that it would be necessary to undertake between twenty and thirty reaction steps to accomplish their successful synthesis.

II. Vinylsilanes.

Triallyl and triphenylvinylsilane were prepared by reacting the corresponding Grignard reagent with trichlorovinylsilane.



Allyl magnesium chloride did not appear to be as readily soluble in ether as other Grignard reagents.

Hence the preparation of the triallylvinylsilane required a highly diluted ether solution of the Grignard reagent.

The elemental analysis of the triallylvinylsilane was low in carbon. However, it has been confirmed (38) that carbon analyses on relatively volatile organo-silanes usually exhibit low carbon values.

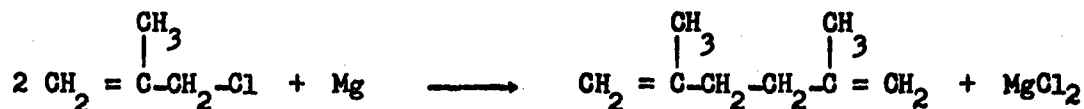
The triallylvinylsilane is quite stable and has a definite boiling point of 65-66°C/7mm. or 49-51°C/2mm. This material would not polymerize by itself when treated with benzoyl peroxide for extended periods at elevated temperatures. In this respect, it resembles triallylpropylene, which does not polymerize by itself with peroxide type catalysts. The compound readily decomposed potassium permanganate solution and decolorized bromine in carbon tetrachloride solution. No solid derivatives could be made either by bromination or oxidation.

In the work on triphenylvinylsilane no product could be isolated when the trichlorovinylsilane was added to the Grignard reagent. If the procedure was reversed, a small amount of product was obtained, although a fair quantity of biphenyl was also formed. A mid-fraction consisting of a viscous oil was obtained but not identified. These results were in substantial agreement with the observations of Cason and Brooks (39).

Trimethylvinylsilane was prepared but in so small a yield that distillation of the product could not be carried out.

The methallyl Grignard reagent could not be prepared and, therefore, the attempt to prepare trimethallylvinylsilane failed. The reaction

of methallyl chloride with magnesium produced 2,5-dimethylhexadiene-1,5. Schales (40), in an attempt to prepare the methallyl Grignard, also found that the only product was the hexadiene.



An attempt to prepare trisubstituted tert.-butylvinylsilane failed. The tert.-butyl Grignard reagent did not react with trichlorovinylsilane. The size of the tert.-butyl group probably sterically limits such groupings to three about the central silicon atom. The polymerized residue that was produced in this instance may have come from hydrolysis of the mono- and di-substituted products. It was assumed that the unreacted chlorine on the mono- and di-substituted compound was hydrolyzed to the corresponding silanol during the water wash. These silanols are very temperature sensitive and polymerize when distillation is attempted.

It is well known that cyano groups present in a polymeric material usually enhance its oil resistance. Because of this, it was desired to prepare some vinylsilanes that would contain these cyano groups.

Attempted methods of introducing the cyano group on trichlorovinylsilane by substitution of the chlorine atom included reactions with sodium cyanide, silver cyanide, and cuprous cyanide. In each case no reaction was obtained.

The absence of any reaction of trichlorosilane with these various metal cyanides is surprising since alkylchlorosilanes react exothermically with anhydrous sodium acetate in an inert diluent to give the corresponding alkylsilylacetates (41).

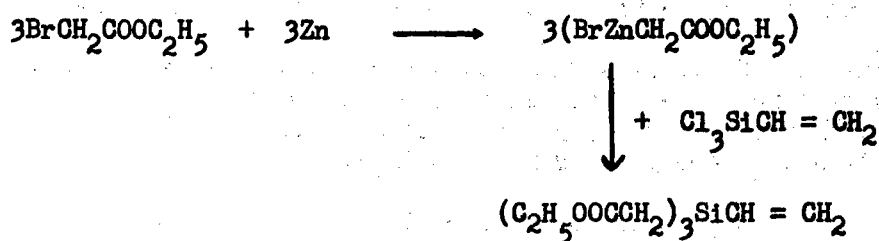
Reported results (42) of a recent study of the products obtained by the reaction of silver cyanide with methylhalosilanes indicated that the formation of isocyanides was the main reaction. The compounds were found to be very easily hydrolyzed. The susceptibility of the diisocyanide to hydrolysis was greater than that of the monoisocyanide. No yields of the attempted synthesis of the triisocyanide and the tetraisocyanide were reported. The reaction of silver cyanide with silyl iodide has been reported (43) to proceed explosively in the liquid phase. The resulting products are silver iodide plus a brown polymeric solid.

It has been concluded that the tricyanovinylsilane would be too unstable a molecule to isolate in its monomeric form. Therefore, further work on attempted synthesis was abandoned.

Attempts were made to place other polar groups, such as the trichloromethyl and the ethyl aceto, on the silicon atom.

Introduction of trichloromethyl groups into the silane unit has been attempted by the Grignard reaction. The formation of the Grignard complex of trichloromethyl magnesium bromide and its subsequent reaction with trichlorovinylsilane was not successfully carried out. Approximately 50% of the starting material, bromotrichloromethane, was recovered. The remainder of the reaction mass gradually assumed a polymeric nature as heating was prolonged. There was no fraction recovered that indicated the formation of hexachloroethane.

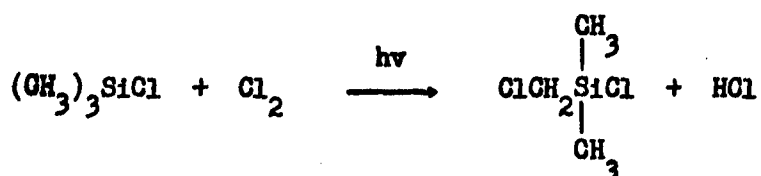
A modified Reformatsky type reaction was used in an attempt to replace the chlorine groups of trichlorovinylsilane with carbethoxymethyl groups:



The addition of the trichlorovinylsilane - ethyl bromoacetate mixture to zinc amalgam resulted in a very vigorous reaction. A sweet-smelling, ester-like material was noted as a product of the reaction. This material readily polymerized during an attempt to isolate it in a pure form.

III. Methylene-silanes

In the attempt to prepare substituted methylene-silanes, a probable starting point in the synthesis is the chloromethyl-dimethylchlorosilane. As was pointed out above, the chlorination of trimethylchlorosilane gives good yields of the desired product.



Several authors have found that the reaction of beta-haloethers with metals results in the formation of olefins. Thus Wislicenus (44) found that one of the products formed by heating chloroacetal with sodium was ethyl vinyl ether. The Grignard reagent from beta-bromophenetole and magnesium decomposes to ethylene (45). Wohl and Berthold (46) noted the formation of ethylene when beta-chlorophenetole was treated with sodium. The reaction of substituted beta-bromoethers with magnesium or zinc has been used by Boord, et al. as a general method for the preparation of olefins of unambiguous structure (47).

The general reaction of this Boord olefin synthesis, where X is halogen, and R and R' are alkyl groups, is as follows:



If the action of metals on silicon compounds with an alpha-haloalkyl group and an alkoxy group attached to the same silicon atom should follow a parallel course, the formation of a silicon-carbon double bond would result. To test this possibility, chloromethyldimethylmethoxy-silane was synthesized. The product was fractionated through a Vigreux

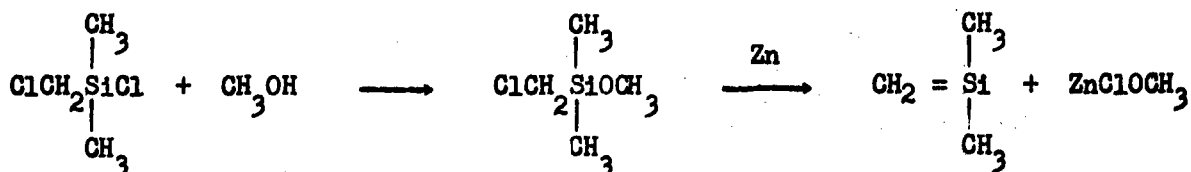
column. The fraction from 119-120°C was redistilled through the same column and a center fraction, boiling point 120°C, was submitted for analysis:

Calc'd, $C_4H_{11}SiClO$: Cl; 25.57. Found: Cl; 27.6; 27.8.

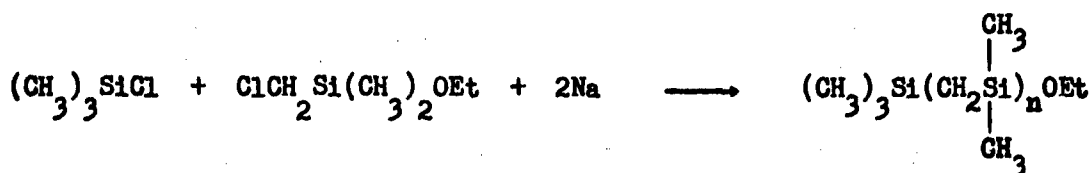
The high value for chlorine could be attributed to either unreacted starting material, $ClCH_2Si(CH_3)_2Cl$ or to the presence of dichloromethoxysilanes $(ClCH_2)_2(CH_3)SiOCH_3$ and $(Cl_2CH)(CH_3)_2SiOCH_3$ as impurities.

Because of this high value in chlorine analysis, it was decided to re-run the experiment and perform a more careful fractionation of the reaction mixture. A larger reaction was made and it was found that refluxing the mixture for two hours improved the yield. On very close fractionation a material was obtained that has the correct chlorine analysis for chloromethyldimethylmethoxysilane. The fact that no easily hydrolyzable chlorine was found in this material as compared to silanes, which have the chlorine attached to the silicon, gives further proof that the chlorine still resides on the carbon atom and not on the silicon.

The following equation illustrates the desired reaction to afford dimethylmethylenesilane:



It is possible that, in the case of the silicon compounds, the reaction may take a different course with the formation of linear polymers rather than silicon-carbon double bonds. Chloromethyldimethylethoxysilane has been condensed with trimethylchlorosilane in the presence of sodium to form methylene-linked silanes (48,49,50).



(n = 1-4)

A paper by Warrick and coworkers (51) and a patent (49) mention that chloromethyldimethylchlorosilane polymerizes when sodium is added to give linear methylene silanes of one to four links to each polymeric chain. Mention is also made that other metals besides sodium would cause the same result. It thus appeared that the dehalogenation of chloromethyldimethylchlorosilane with zinc would probably not proceed as had been originally outlined.

Gilman and Dunn (52) discuss the possibility of the existence of a carbon-silicon double bond. Their conclusions were that it is highly improbable that a structure of this nature could be prepared. Besides steric factors arising from the size of the silicon atom, there is the fact that silicon has less tendency to enter into resonance stabilized structures.

"It is logical to attribute this decreased resonanceto a reluctance of the silicon-carbon bond to assume any double bond character." (52)

In addition to the desired reaction there are at least two other important paths the reaction may take. A normal Grignard reagent may be formed which, unlike the analogous carbon compound, may be stable because of the difficulty of forming the carbon-silicon double bond. Another possibility is the formation of linear polymers such as have already been made from chloromethyldimethylethoxysilane by heating under reflux with sodium (53).

It was anticipated that no difficulty would be encountered in effecting a reaction of the above chloromethylsilane with magnesium since the Grignard reagent from chloromethyltrimethylsilane is readily formed (54). A small trial experiment indicated that this expectation was justified. A small amount of ether and chloromethyldimethylmethoxysilane was added to

magnesium turnings. No reaction was observed until a small amount of freshly prepared methyl magnesium iodide solution was added. A reaction then took place with the separation of a white powdery precipitate.

Chloromethyldimethylmethoxysilane was reacted with magnesium turnings in ether and with zinc dust in isopropanol. No evidence of the formation of dimethylmethylenesilane was obtained. In the reaction with magnesium, in addition to starting material, a product was isolated which had a boiling point (105-10°C/43 mm.) in the range where a dimeric product might be expected to boil. In working up the reaction mixture from the zinc dust preparation, there were indications that interchange of alkoxy groups attached to silicon took place. The desired product $(CH_3)_2Si = CH_2$ corresponds to isobutene with one carbon atom replaced by silicon. Since isobutene boils at -6°C, it was expected that the silicon analog would boil at roughly 0°C.

This phase of the contract was discontinued because it failed to show promise; however, samples of dimethyl-(chloromethyl)-chlorosilane, methyl-(dichloromethyl)-chlorosilane, and dimethyl-(dichloromethyl)-chlorosilane were submitted to Wright Air Development Center.

IV. Allyl Sulfide:

Note: In the preparation of these sulfides it was necessary to handle chloroethyl sulfides, which are mustard type compounds, and which must be handled with extreme care. Both Dr. Halpern and Mr. Laskin of this Laboratory were badly burned when they accidentally came in contact with these compounds. This occurred despite the fact that all necessary precautions were taken to prevent such body contact.

Allyl 2-hydroxyethyl sulfide was prepared by treating allyl mercaptan with ethylene chlorohydrin in the presence of sodium methylate. Treatment of the resulting product with concentrated hydrochloric acid yielded 2-chloroethyl allyl sulfide.

When the attempt to dehydrohalogenate the 2-chloroethyl allyl sulfide was made, only volatile, gaseous sulfide products were obtained. The same resulted when quinoline was used as the dehydrohalogenating agent. One would expect, however, that allyl vinyl sulfide should have physical properties similar to those of divinyl sulfide. This was not found to be the case.

V. Divinyl Sulfide

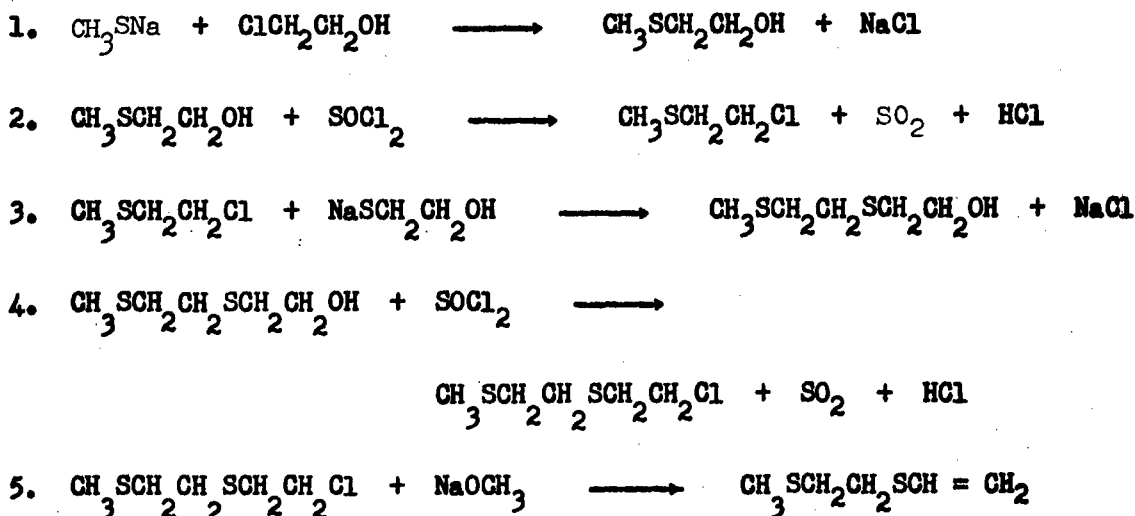
Divinyl sulfide was made in good yield by the dehydrohalogenation of mustard gas. Despite its higher boiling point, when prepared in methanol it distilled in about a 1:1 ratio with the methanol. The method used was essentially that described by Bales and Nicholson (27).



Samples of this product were submitted to Wright Air Development Center.

VI. 2-(Methylthio)-ethyl Vinyl Sulfide

The reaction scheme for the preparation of 2-(methylthio)-ethyl vinyl sulfide followed in this preparation was:



Reaction (1) was carried out by the method described in Organic Syntheses (55) with some modifications, including the use of methyl mercaptan from a cylinder instead of from the decomposition of methyl isothioureia sulfate in alkali. The procedure for reaction (2) was also a modified version of Organic Syntheses (56). For reaction (3), the procedure followed was that described by R.G. Brown and R. C. G. Moggridge (57). The latter reference also covers reactions (4) and (5). Reaction (4) also has been carried out by Goldsworthy, (58), who isolated the product by merely removing the solvent under vacuum instead of distilling it as did Brown and Moggridge.

In carrying out this reaction sequence it was found important to use rigorously purified thionyl chloride in the preparation of 2-(methylthio)-ethyl 2'-hydroxyethyl sulfide (step 4).

Cottle (59) recommends that thionyl chloride be refluxed over flowers of sulfur and then be fractionally distilled to accomplish the required purification. This procedure was found quite suitable, particularly when the distillation was carried out with a Fenske column.

In the dehydrohalogenation (step 5) it was found that two changes in conditions were necessary to obtain a product. The substitution of ether for chloroform reduced the reaction temperature and, thus, minimized the formation of complicating tars. The addition of a small amount of pyridine catalyzed the decomposition of the intermediate. A small trial synthesis was successfully made using these modifications. This was followed by an equally successful large run and the sample was submitted to the Wright Air Development Center.

The boiling point of the material submitted, 82.5°C/5 mm., was reasonably close to 65°C/2 mm. which was the only data reported in the literature (57).

On receipt of a report from Wright Air Development Center that the compound did not polymerize and that infrared examination indicated that no vinyl groups were present, a sample was sent out for elementary analysis. The results confirmed the infrared analysis.

	% C	% H	% S	
Calc'd for $C_5H_{10}S_2$	44.73	7.51	44.77	(Vinyl Cpd)
Calc'd for $C_6H_{14}S_2O$	43.33	8.48	38.55	(Methoxyl Cpd)
Found	42.6	8.3	38.8	

The analytical values, with the exception of a small discrepancy in the value for carbon, check closely with the calculated figures for 2-methylthioethyl 2'-methoxyethyl sulfide. The formation of methoxyl compound under the conditions of the reaction is not too startling since the reaction of a sodium alkoxide with an alkyl chloride to form an ether is the basis of the well-known Williamson ether synthesis.

Unfortunately, there is no simple chemical method for determining unsaturation in sulfides. Brown and Moggridge state that the methylthioethyl vinyl sulfide they obtained showed no tendency to polymerize.

Failure to take part in polymerization reactions, however, is not necessarily a criterion for the presence of a vinyl group. The usual methods of demonstrating unsaturation are made useless by the presence of the sulfide linkages which undergo oxidation and form addition compounds with halides. Even catalytic hydrogenation might be ineffective because of poisoning of the catalyst. The only obvious methods for determining composition in this case are elementary analysis and infrared examination.

At the time the preparation was carried out the following fractions had been obtained:

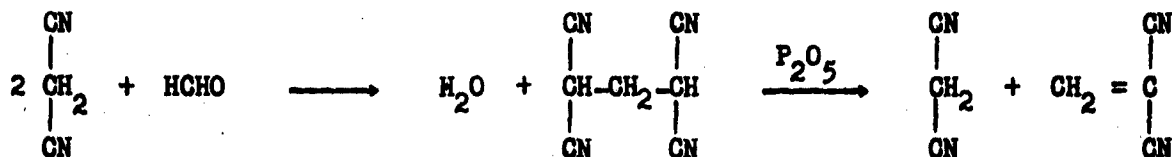
Fraction	Boiling Point ° C.	Weight, g.
I	52-62°C/5 mm.	55.7
II	62-82°C/5 mm.	5.2
III	82-85°C/5 mm.	108.6

Fraction III, being the major component, had been submitted. Re-examination of Fraction I, however, showed that this was the desired monomer. It was a re-distilled portion of Fraction I, which was finally submitted to the Wright Air Development Center.

VII. Vinylidene Cyanide.

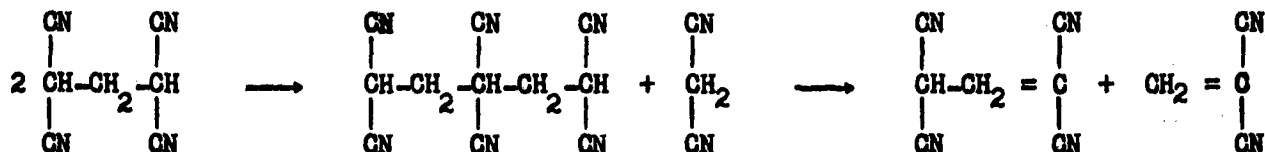
Judging from the literature, the best method for the preparation of this monomer appeared to be the thermal decomposition of 1,1,3,3-tetracyanopropane as described by Ardis *et al.* (60).

Since the directions given by Diels and Conn (61) for the preparation of tetracyanopropane by the condensation of malononitrile with formaldehyde are not very specific, several small trial runs were made. Trials were conducted using 4 gram samples of malononitrile with both methanol and water as solvents. On the basis of these trials larger preparations were carried out.



Ardis, *et al.* (60) indicate that vinylidene cyanide is very unstable in the presence of water. Special care was used so that the reaction set-ups were kept as dry as possible.

It was also found that the higher homologs of the reaction of malononitrile with formaldehyde; namely, 1,1,3,3,5,5-hexacyanopentane, could be decomposed to vinylidene cyanide by the above method.



In the early preparation of tetracyanopropane, it had been found impossible to obtain products free of high melting impurities. In some cases, the entire product had become insoluble during recrystallization.

The possibility that this difficulty was caused by the pH of the solution during crystallization was considered.

Samples were recrystallized from acetonitrile in which an acid pH was maintained by the addition of small amounts of phosphorus pentoxide. No difficulty with formation of insoluble, high-melting products was experienced with this method of crystallization.

The product was very white and exhibited no tendencies to darken upon standing. It seems, therefore, that a slightly acid condition is needed to store the tetracyanopropane.

In the initial attempts to decompose the tetracyanopropane to vinylidene cyanide a great deal of polymer formation was observed. This was thought to be due to a recombination of vinylidene cyanide and malononitrile. A slightly acidic condition, it was reasoned, should alleviate this side product. Accordingly, phosphorus pentoxide powder was liberally sprinkled throughout the entire apparatus. In this way an acidic medium was insured at all points of contact. It was found that using this technique a very good yield of highly purified vinylidene cyanide could be prepared.

Vinylidene cyanide appears to be odorless. Yet even very small traces were detectable in the atmosphere because of the intensely irritating effect on the mucous membranes of the eyes, nose, and throat. The respiratory system was also affected. One of the laboratory personnel had to be hospitalized from congestion of the lungs and symptoms similar to asthma on exposure to very small amounts of this compound.

A sample of vinylidene cyanide was submitted to Wright Air Development Center.

VIII. N-(2,2,2-Trifluoroethyl)-acrylamide

The method of preparation of N-(2,2,2-trifluoroethyl)-acrylamide is essentially the same as that used for the preparation of N-alkyl-N-(1,1-dihydroheptafluorobutyl)-acrylamide. Consequently, for a discussion of the synthesis the reader is referred to Section XII below.

Briefly, trifluoroacetic acid was esterified with methanol. The ester was subjected to ammonolysis to the amide. Trifluoroacetamide was reduced with lithium aluminum hydride to yield 2,2,2-trifluoroethylamine salts. This product was found in the solid phase of the reaction products as well as in the acidulated water layer.

The free amine was prepared by treating the salt with alkali. The acrylamide was easily formed by treatment of the amine with acrylyl chloride.

This acrylamide was found to be more unstable than the 1,1-dihydroheptafluorobutylacrylamide. The tendency to polymerize in solution was much greater.

IX. 1,1-Dihydroheptafluoro-1-butyl alpha-(Trifluoromethyl)-acrylate

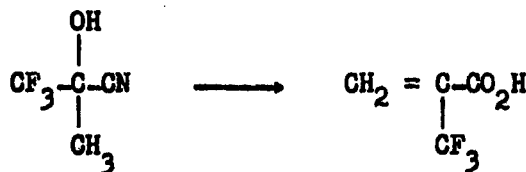
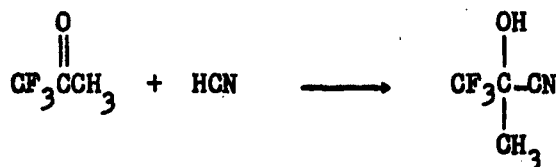
Esterifications of both heptafluorobutyric acid and trifluoroacetic acid were carried out by standard procedures.

Part of the methyl heptafluorobutyrate was required for the preparation of 1,1-dihydroheptafluoro-1-butanol by lithium aluminum hydride reduction. The yields from this reaction were quite good and free of heptafluoro-1-butanal. This particular procedure is believed to be novel.

Methyl perfluoroacetate was prepared in kilogram amounts for conversion to trifluoroacetone by use of the mixed Claisen condensation of esters:



The trifluoroacetone was to be converted to its cyanohydrin and later hydrolyzed to the acid:



In subsequent research on trifluoroacetone cyanohydrin, a new commercial source of the compound was used.

Methyl alpha-(Trifluoromethyl)-acrylate

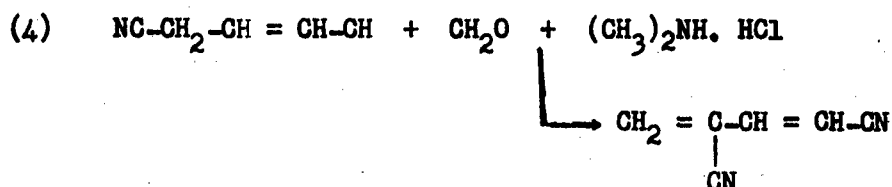
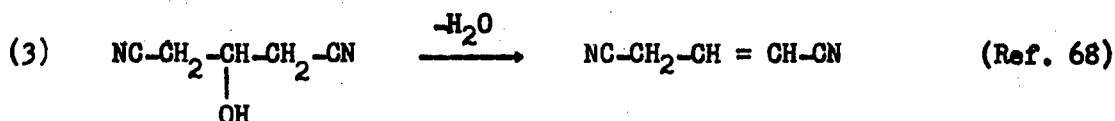
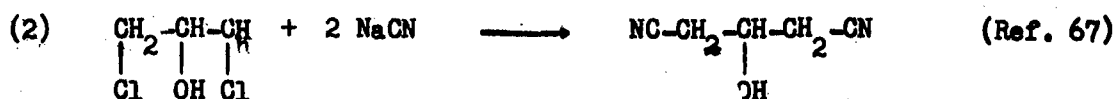
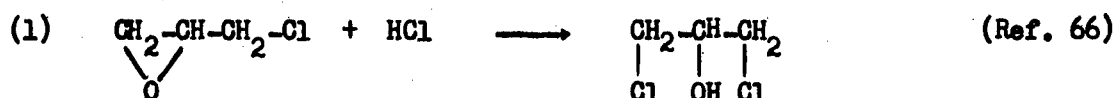
The details of the method of converting acetone cyanohydrin to methyl methacrylate by treatment with sulfuric acid and methanol are well-known. Application of two modifications of this method to trifluoroacetone cyanohydrin resulted only in the formation of the related hydroxy ester.

The difficulty in dehydrating to the acrylic ester is not too surprising, although Haszeldine and Sharpe (62), on the basis of a private communication from Darrall and Smith, state that d,l-trifluoromethyl lactic acid, on treatment with strong sulfuric acid and subsequent esterification gives methyl alpha-(trifluoromethyl)-acrylate.

The strong inductive effect of the trifluoromethyl group would be expected to decrease the tendency of the hydroxyl group to add a proton as a preliminary step towards dehydration. Previous investigators have indeed found that 1,1,1-trifluoro-2-octanol, 1,1,1-trifluoro-2-pentanol (63), and ethyl beta-hydroxy-gamma, gamma, gamma-trifluorobutyrate (64) were extremely difficult to dehydrate. The first two alcohols were converted to the corresponding olefins, by pyrolysis of the acetates at 500°C, after several other methods had failed. The hydroxy ester was finally converted to the unsaturated compound by the boric anhydride procedure of Brandenberger and Galat (65).

X. 1,3-Dicyano-1,3 butadiene.

A survey of the chemical literature indicated that the desired monomeric material, 1,3-dicyano-1,3-butadiene, has not yet been prepared. Of a number of possible syntheses, the following sequence of reactions was selected initially because all steps of the reaction, except the last one, had been reported, and because the starting materials were available:



Step (4) in this scheme is based on the fact that 1,3-dicyano-1-propene, as anticipated by theory, contains an active methylene group comparable to that in malononitrile (68). By means of one of several reactions, such as the Mannich reaction indicated herein, the synthesis of the desired 1,3-dicyano-1,3-butadiene may be completed.

Although the literature (67,68) reports the preparation of the 1,3-dicyano-3-propanol as indicated, no yields nor working conditions were given.

A few attempts were made to convert the dichloropropanol to the dicyano derivative, but no product could be isolated. The vigor of the reaction in all cases indicated that a definite reaction was taking place, but on attempted isolation only tarry and carbonaceous residues remained.

In view of the difficulty experienced previously with the isolation of 1,3-dicyano-2-propanol from an aqueous reaction medium, an attempt was made to run the reaction in the absence of water and by using cuprous cyanide instead of sodium cyanide.

The first phase of this synthesis involved the use of methanol as a solvent. After approximately fifteen hours of refluxing 1,3-dichloro-2-propanol with cuprous cyanide in methanol, no evidence of reaction could be found. Thereupon, the solvent was distilled out, and reaction was forced at much higher temperatures.

To isolate a product from the resulting mixture, acetylation was resorted to. This resulted only in the recovery of a portion of the starting carbinol in the form of the acetate ester. Consequently, this particular synthesis was abandoned.

One simple modification of this preparation involves the use of the acetate of dichloropropanol. This approach seemed to have the added advantage of involving materials that were less water soluble than those having a free hydroxyl group.

Prior to an attempt to prepare 1,3-dicyanopropyl acetate, three different methods were used to obtain the starting material, 1,3-dichloro-2-propyl acetate. These were: acetylation of 1,3-dichloro-2-propanol with acetic anhydride in the presence of sodium acetate, a similar acetylation in the presence of "mixed alkane sulfonic acids, and a Fischer esterification of the carbinol with acetic acid in the presence of "mixed alkane sulfonic acids". All of these methods afford adequate yields of the desired ester, although the last mentioned synthesis appears to be accompanied by the formation of substantial quantities of an unidentified, high-boiling side product.

A three-mole preparation of 1,3-dichloro-2-propyl acetate was thereupon carried out. The final distillation of the product revealed the presence not only of the desired, known product (b.p. 198-198.5°C/ at 748.5 mm., 70-71°C/ at 1mm.) but also of a substantial quantity of a high boiling side product (b.p. 229-235°C/ at approximately 750 mm., 74-87°C/ at 1mm.). The nature of this product was not determined but it may well be the same as the compound with an empirical formula $C_6H_8Cl_4$ isolated by Schmerling.

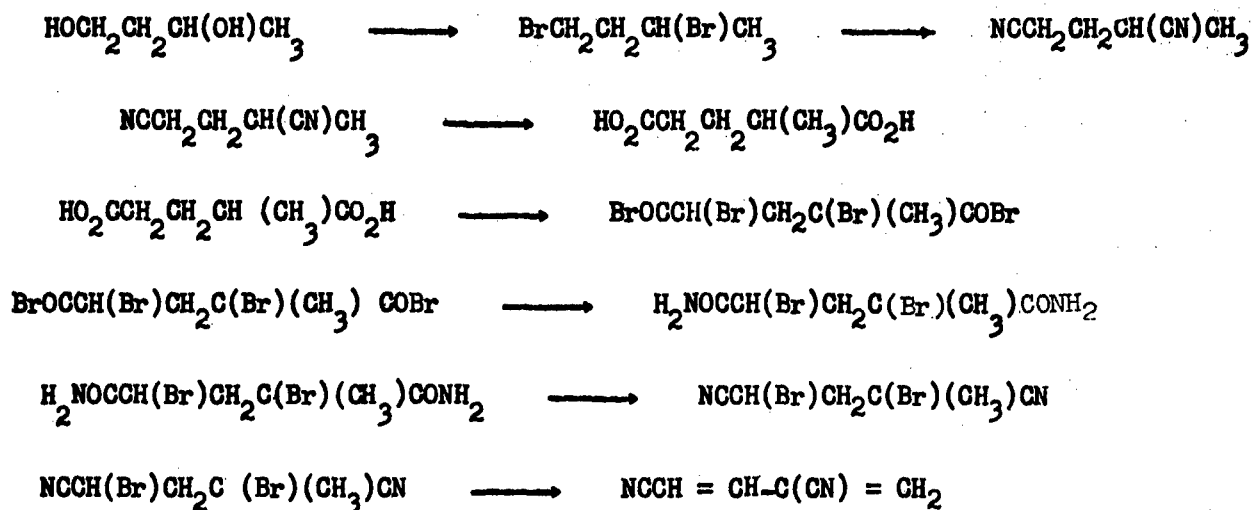
The first attempt at the preparation of 1,3-dicyano-2-propyl acetate was carried out with an excess of sodium cyanide dissolved in water to which a methanol solution of the dichloro ester was added. This reaction proved very exothermic. A continuous extraction of the reaction product with ether did not seem to be particularly effective. Steam distillation of aqueous residue afforded only a trace of a yellow oil.

In a second effort, an excess of 1,3-dichloro-2-propyl acetate was gradually added to an aqueous solution of sodium cyanide containing a catalytic amount of potassium iodide (following recommendations of Legrand (68)). From an extract of the reaction mixture, which had been purposely designed to be saturated with respect to sodium chloride at the end of the reaction, with acetonitrile, a solid had been isolated which could be sublimed.

It was observed that the distillation of the acetonitrile solution left as a residue, not only this sublimable solid, but also another hard, intractable solid which could not be redissolved in acetonitrile. Consequently, it seemed possible that this latter solid formed during the distillation. Two other attempts at substituting two nitrile groups for the chloro groups of the acetate were carried out. The reaction conditions used were very similar to those previously tried and the usual exothermic character of the reaction was noted as well as a strong darkening of the reacting system. The first of these reaction mixtures was extracted continuously over a period of several days with acetonitrile as a solvent. The other reaction product was extracted continuously with ethyl acetate. Neither of these solvents appeared to be particularly effective.

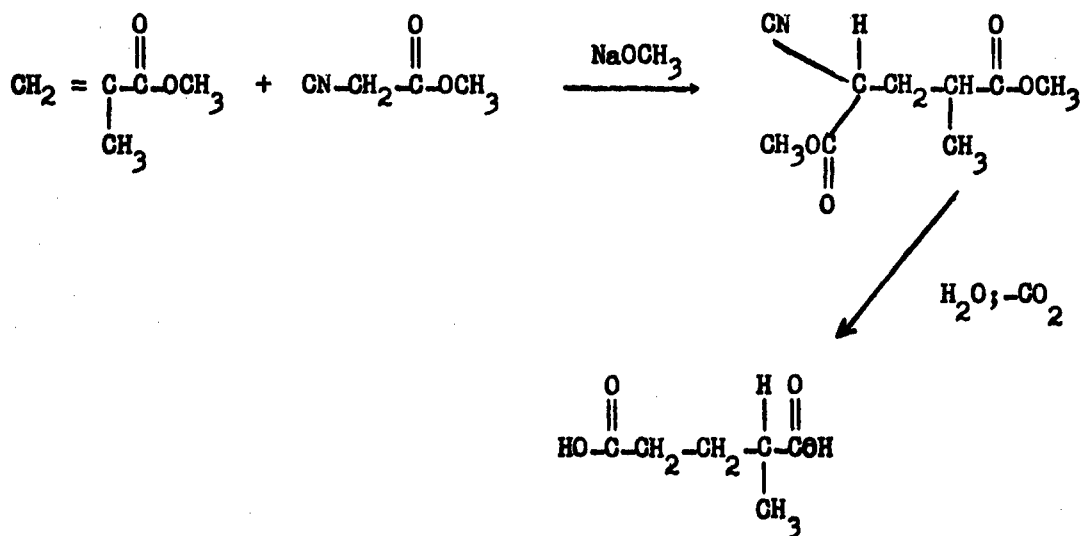
In general, the work on the preparation of 1,3-dicyanopropene has not been too successful. Since the ultimate objective of this project was the preparation of 1,3-dicyano-1,3-butadiene, other methods had to be explored.

Among the alternative synthetic routes was one involving the conversion of 1,3-dibromobutane to the corresponding dinitrile. Hydrolysis of the dinitrile to alpha-methylglutaric acid was to be followed by a Hell-Volhard-Zelinsky bromination to the 1-methyl-1,3-dibromoglutaryl bromide. Di-ammoniation of this acyl bromide followed by dehydration should afford a product which, on dehydrohalogenation, affords 1,3-dicyano-1,3-butadiene:

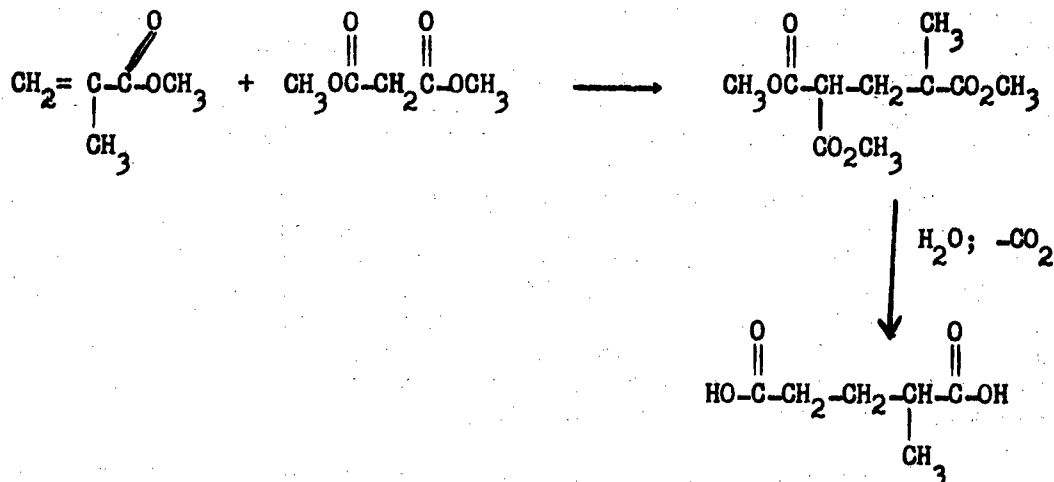


Since alpha-methylglutaric acid could be prepared by methods other than from 1,3-dibromopropane, effort was concentrated on synthesis of the acid.

The literature mentions one suitable procedure which involves the Michael condensation of methyl methacrylate with methyl cyanoacetate in the presence of sodium alkoxide (69). The product is then hydrolyzed and decarboxylated to yield alpha-methylglutaric acid.



An alternate route involves the condensation of methyl methacrylate with dimethyl malonate. The intermediate product is closely related to that described in the first condensation. The alpha-methylglutaric acid is obtained by hydrolysis and decarboxylation.



Both condensations were attempted to determine which would be the more convenient route to the required amounts of alpha-methylglutaric acid.

A third attempt was made to prepare alpha-methylglutaric acid by the condensation of methyl methacrylate with ethyl cyanoacetate in the presence of sodium methoxide. In this particular experiment, the sodium methoxide was prepared freshly from sodium and absolute methanol whereas in the previous case commercially available sodium methoxide had been used. In this experiment particular attention had been paid to start with anhydrous reagents. As in previous cases, the final product turned out to be an oily material.

The oily products from the three experimental preparations were separately worked up. The final oils from each procedure crystallized very slowly after several weeks of standing. The purity of these products was not particularly high, although it was thought suitable for further synthetic steps.

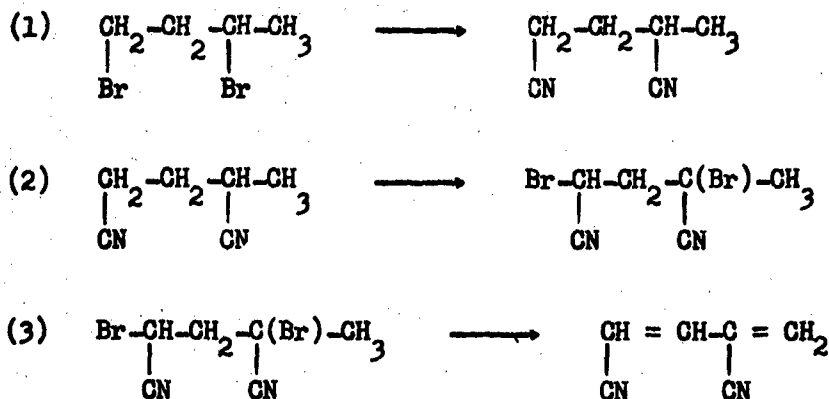
The crude alpha-methylglutaric acid available to us was subjected to a Hell-Volhard-Zelinsky reaction.

The typical examples of this reaction, as described in the literature (see, for example, reference 70), involve the treatment of a dispersion of red phosphorus in a liquid carboxylic acid with bromine. Since our acid was a solid, it was considered advisable to modify the conditions by using an indifferent solvent, such as benzene, as the reaction medium. This proved quite successful. The reaction proceeded quite smoothly, although it was found to be exothermic in character.

Distillation of the product gave a main fraction, b.p. 75-78°C/14 mm. which suddenly solidified in the distillation head and in the fractionating column during distillation. As a result, the distillation flask was forcibly separated from the column by the ensuing pressure. To bring relief to the laboratory from the copious hydrogen bromide fumes, the apparatus had to be sprayed with water. Although attempts were made to continue the purification of the residues, the water treatment had completely ruined this preparative attempt.

Termination of the contract prevented further experiments along this line.

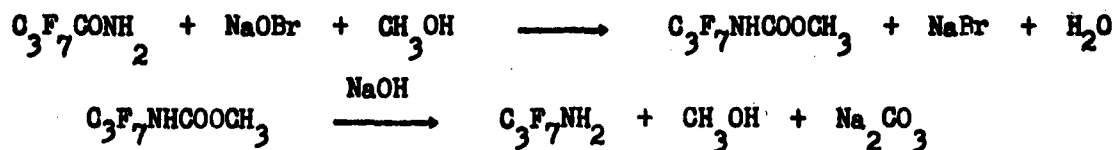
Since 1,3-dibromobutane was available, a few brief attempts were made to prepare 1,3-dicyanobutane as an intermediate in the following reaction sequence:



The attempt to prepare 1,3-dicyanobutane from 1,3-dibromobutane and silver cyanide in an aromatic solvent failed completely. This was attributed to the extreme insolubility of the cyanide.

XI. Heptafluoropropylamide

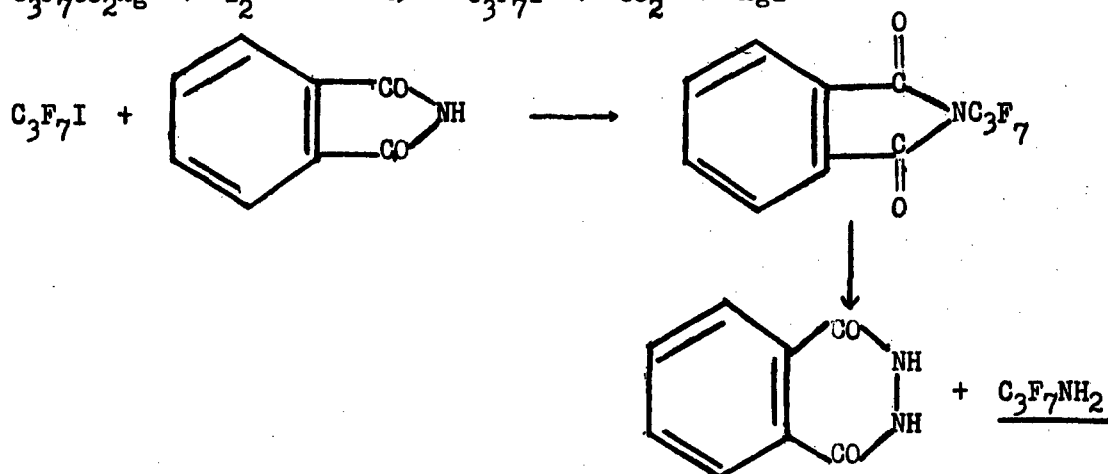
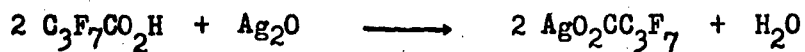
An attempt was made to prepare heptafluoropropylamine from the heptafluorobutyramide using a Hofmann hypobromite rearrangement.



Almost a quantitative yield of starting material was obtained, indicating that rearrangement had not occurred. Wallis and Lane (71), in discussing the mechanism of the Hofmann rearrangement, mention that electron withdrawing groups tend to inhibit the reaction. In this particular fluoroamide the seven fluorine atoms must undoubtedly have a powerful electron withdrawing tendency, leaving the nitrogen atom fairly electropositive.

A Curtius rearrangement (72) was also attempted. The hydrazide of perfluorobutyric acid was prepared by reacting hydrazine hydrate with the methyl ester of perfluorobutyric acid. This, when treated with nitrous acid and heated in methanol, gave what appeared to be the perfluoro-*syn*-propylurea.

In view of the difficulties encountered in the preparation of heptafluoropropylamine, it was decided to attempt the preparation of this compound by the Ing-Manske amine synthesis. Using available starting materials, the proposed reaction scheme was the following:



The method for the preparation of the silver salt of the perfluorobutyric acid given in the literature (73) was modified. The use of benzene as a solvent for the silver salt and as a water entrainer made isolation of this silver salt an easy task.

Several batches of silver perfluorobutyrate were prepared in very good yields. One batch gave a product which showed no deterioration on prolonged exposure to light.

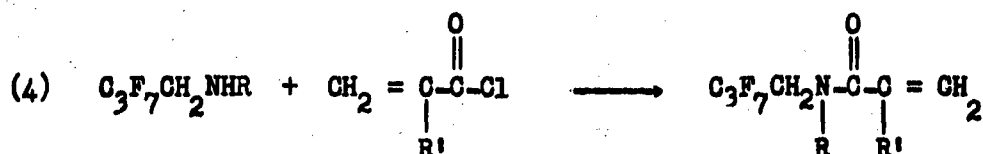
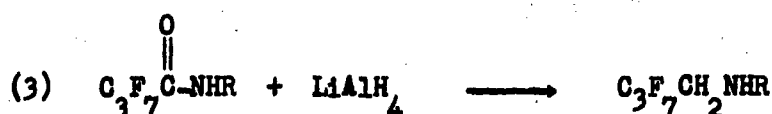
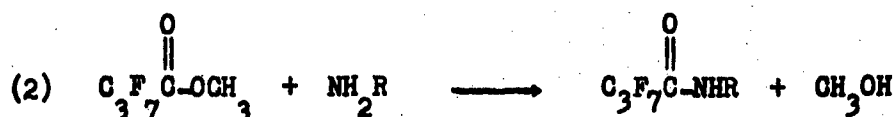
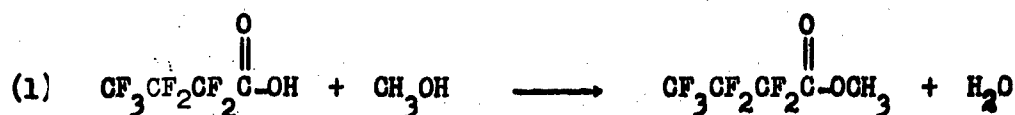
Preparation of 1-iodoperfluoropropane from silver perfluorobutyrate

Four preparations were carried out according to the literature directions (Hauptschein and Grosse (73)). The average yields in these preparations were approximately 50%. Our total stock of 1-iodoperfluoropropane was combined and purified by fractional distillation. The fractions boiling between 40.6 and 44.4°C were combined and preserved in a sealed ampoule.

Several exploratory preparations of N-perfluoropropylphthalimide were carried out. Results were inconclusive.

XII. N-Alkyl-N-1,1-dihydroheptafluorobutylacrylamides and
N-Alkyl-N-1,1-dihydroheptafluorobutylmethacrylamides.

The reaction sequence for the preparation of these monomers was the following:



Where -R = H-, alkyl-, or C₃F₇CH₂-; and -R' = H- or CH₃-

Direct reaction of heptafluorobutyric acid with methanol gave the desired ester quite readily. The treatment of the ester with ammonia or an amine followed the method of Gilman and Jones (74). The reduction with lithium aluminum hydride initially followed the procedure of Nystrom and Brown (75); however more adequate yields and easier manipulation was achieved by modifications indicated in the experimental section.

The formation of the acrylate or methacrylate was usually carried out in the presence of triethylamine which reacted with the hydrogen chloride generated during the reaction.

Special attention must be given to the matter of lithium aluminum hydride reductions.

In one attempt to reduce N-ethylheptafluorobutyramide to the corresponding amine with lithium aluminum hydride, a serious fire took place which brought about a total loss of product. Conversation with the technical staff of Metal Hydrides, Inc. has indicated that somewhat similar experiences have been reported by the Minnesota Mining & Manufacturing Company when the latter worked with the reduction of certain fluoro-compounds.

Minnesota Mining & Manufacturing Company reported that, during the reduction of perfluorosuccinamide, a serious explosion took place.

The reaction of this laboratory was carried out during a day on which the temperature in the laboratory was well over 100°F. There is the possibility that the fire may have been caused by these unusual climatic conditions.

The fire occurred after all the lithium aluminum hydride had been added to the ether, the reduction had been nearly completed, and the mixture was being brought to reflux with an infrared lamp. During the reaction, the high ambient temperature had made it nearly impossible to keep ether in the flask even though several condensers were in series. Several ether additions had been made to keep the mixture fluid. Despite this, the reaction mixture seemed to be more gelled than usual. Metal Hydrides, Inc. however, does not consider this condition abnormal.

After the fire had been brought under control, the decomposition of the reaction mixture occurred in a very spectacular manner. Once the reaction had gotten under way, it spewed forth a gas with an amine-like odor.

Metal Hydrides, Inc. cautioned against the use of such large quantities as we had been using in the past. The particular run which ignited involved the use of approximately eight moles of lithium aluminum hydride; whereas Metal Hydrides, Inc. recommends that no more than three moles be used in ordinary laboratory equipment. This recommendation was followed in subsequent preparations at this Laboratory. It has also become the practice to specify that at least 2-l. of anhydrous ether be present in the reaction flask at the end of the reduction for every 100 g. of reducing agent initially utilized.

If the reaction mixture was to be heated, a water bath (warm) was used in such a manner that the water level was maintained below the level

of the reacting solution. In this manner the rate of the heating was kept under control and the possibility of accidentally heating dried out droplets of material on the walls of the flask was eliminated.

Once the reduction was considered over, the excess of lithium aluminum hydride was reacted with an excess of anhydrous ethyl acetate rather than water. Thus another potential hazard was eliminated.

The yields of the free amines liberated from the bisulfates formed at the end of the reduction proved to be low. Despite great care in using equipment that would be capable of readily condensing low boiling liquids, yields of the free base were on the order of 10 to 20 per cent of theory (based on the quantity of butyramide reduced with lithium aluminum hydride). The cause of this low yield could not be determined with any high degree of certainty, although evidence was found that the reduction of perfluorinated amides was incomplete in the time allotted for reaction.

In later modification of the reaction, the lithium aluminum hydride reduced mixture was hydrolyzed on the alkaline side. The amine could then be isolated directly from the ether solution. Yields were greatly improved by this method and unreacted starting material could be recovered.

A number of intermediate materials as well as final monomers were prepared during this phase of the project.

Many of the materials, since they had not been previously reported in the literature, had to be repurified and subjected to elementary analyses. Physical constants were also determined for many of these compounds.

In general, the analyses for carbon, hydrogen, and nitrogen were of a low order of accuracy. Two independent analytical laboratories carried out this work. The cause of this lack of accuracy was associated with a white "sublimate" which formed in the combustion tube and was carried through to the absorption train of the analytical apparatus. The nature of this material is unknown, but it is probable that this interfering material results from the reaction of fluorine-containing compounds with glass at the temperature of the combustion train.

The result of these analyses are given in Table I. Since the quantities of N-alkyl-N-(1,1-dihydroheptafluorobutyl) methacrylamides was quite limited, it was not possible to obtain samples of sufficient purity for analyses. The physical constants reported for this class of compounds must also be considered tentative.

TABLE I

Analyses of Some Fluorine-Containing Compounds

Compounds	%C, Calc.	%C, Found	%H, Calc.	%H, Found	%N, Calc.	%N, Found
N-Alkyl heptafluoro- butyramides						
Methyl	26.4	26.3 26.3	1.8	2.0 2.1	6.2	6.2 6.2
Ethyl	29.9	31.8 29.6	2.5	7.4 2.9	5.8	6.3 6.6
n-Butyl	35.7	35.6	3.8	3.9	5.2	5.3
iso-Butyl	35.7	35.2 35.4	3.8	3.6 4.1	5.2	5.4 5.6
(1,1-Dihydroheptafluorobutyl)	24.3	---- 23.8	0.76	--- 1.3	3.54	4.1 4.3
N-Alkyl-1,1-dihydroheptafluorobutylamines						
Methyl	28.2	28.4	2.8	3.5	6.6	6.9
Ethyl	31.7	32.2	3.6	4.3	6.2	5.9
n-Butyl	37.1	38.4	4.7	5.3	5.5	5.6
iso-Butyl	37.7	39.0 37.8 37.3	4.7	7.3 5.1 4.8	5.5	5.6 6.6 5.7

TABLE I

(continued)

Compounds	%C, Calc.	%C, Found	%H, Calc.	%H, Found	%N, Calc.	%N, Found
(1,1-Dihydroheptafluorobutyl	25.2	26.6	1.3	1.7	3.7	3.7
N-Alkyl-N-(1,1-dihydroheptafluorobutyl)acrylamides						
Hydrogen	33.21	33.4	2.4	2.5	5.5	5.6
Methyl	36.0	36.6	3.0	3.8	5.2	5.2
Ethyl	38.4	38.4 38.3	3.6	4.0 4.9	4.9	5.3 4.9
n-Butyl	42.7	43.1	4.6	4.7	4.5	5.0
iso-Butyl	42.7	43.2 43.5 44.0	4.6	4.7 4.8 7.1	4.5	5.0 5.0 4.7

Physical constants of many compounds prepared under this contract are given in Tables II and III.

In general the final distillations of these compounds were carried out on center-cuts from earlier fractionations and involved the use of a 30 cm. by 0.4 cm. "empty tube" micro-fractional distillation column at low through-put. Unless otherwise indicated in the Table, the fraction of material reported upon was a center-cut of constant boiling point.

The tentative nature of physical properties of the N-alkyl-N-(1,1-dihydroheptafluorobutyl) methacrylamides has already been indicated. The refractive indices of the N-n-butyl and N-iso-butyl members of this series are to be considered very approximate since, at room temperature, even the freshly distilled samples had traces of a solid dispersed throughout. The refractive index of 1,1-dihydroheptafluoro-1-butanol was estimated since this constant fell below the calibrated scale of the Abbe refractometer.

TABLE II

Physical Constants of Some N-Alkyl-heptafluorobutyramides

Compounds	Boiling °C	Point mm. Hg.	Melting Point, °C
N-Alkyl heptafluoro- butyramides			
Hydrogen	--	--	107-108°C
Methyl	167°C	756 mm.	43°C (equil.)
Ethyl	168	759	
n-Butyl	192	766	
iso-Butyl	184	761	
(1,1-dihydroheptafluorobutyl)	169	756	59 (equil.)

TABLE III

Physical Constants of Some Fluorine-Containing Compounds

Compounds	Boiling Pt. °C.	mm. Hg.	Refractive index n_D^{20}	Density d_{25} , g./ml.	Am't shipped to WADC
1,1-Dihydrohepta- fluoro-1-butanol	96°	745 mm.	1.2995 (a)	1.576	
N-Alkyl-1,1-dihydrohepta- fluorobutylamines					
Hydrogen	63	746	1.300		
Methyl	83.5	754	1.3076	1.368	
Ethyl	98.5	75.	1.3223	1.188	
n-Butyl	138	754	1.3390	1.223	
iso-Butyl	132	754	1.3379	1.209	
(1,1-Dihydrohepta- fluorobutyl)	137- 137.5	752	1.3000	1.591	
N-Alkyl-N-(1,1-dihydrohep- tafluorobutyl) acryl- amides					
Hydrogen	(e)				

TABLE III

(continued)

Compounds	Boiling Pt. °C. mm. Hg.		Refractive index n_D^{20}	Density d_{25}^4 , g./ml.	Am't Shipped to WADC
Methyl	79	11	(b)	(b)	27.2
Ethyl	95	15	1.3829	1.350	68.3
n-Butyl	112	15	1.3930	1.267	100.0
iso-Butyl	107	15	1.3901		30.5
N-Alkyl-N-(1,1-dihydroheptafluorobutyl) methacrylamides					
Methyl	77	8	1.3763	1.325	16.5
Ethyl	107	29	1.3844 (c)	1.269	13.1
n-Butyl	114	11	1.3906 (d)		13.3
iso-Butyl	90	5	1.3947 (d)		11.2
(1,1-Dihydroheptafluorobutyl) (crude)					5.3

-
- (a) estimated refractive index - see text.
 - (b) solid at room temperature, m.p. appr. 20°C.
 - (c) Refractive index taken at 25°C.
 - (d) Approximate refractive index - see text.
 - (e) m.p. 57.4 - 57.6°C.
-

Attempts were made to prepare the acrylamide and methacrylamide from Di-(1,1-dihydroheptafluorobutyl) amine, but only crude products were isolated in small yields.

Note: The use of rubber gloves and of a gas mask fitted with an "acid" canister is strongly to be recommended while handling acrylyl and methacrylyl chloride solutions, even in a very efficient hood.

XIII. Polymerization Studies

A bottle polymerizer was constructed from an old oscillating type washing machine. It was decided to build the polymerizer in our own shops because a commercially available type was prohibitive in cost with very poor prospects of early delivery. The tub of the machine was insulated, the motor drive removed, and the agitator modified to hold twenty-four four-ounce bottles or six sixteen-ounce bottles.

Initially, when the bath was set up with a 2000 watt heater of small area, some "hunting" was noticed in the temperature as determined by a thermocouple connected to an automatic recording potentiometer. Also there was some temperature variation within the bath at any given time when the heater was on. These difficulties were remedied by calculating the approximate heat loss of the unit from the temperature-time record obtained using the 2000 watt heater, and using this calculated value to determine the capacity of the heater which would maintain the bath at the highest temperature required. A 300 watt immersion heater which extended almost all the way around the tub was installed. This heater, in conjunction with the Fenwal Thermoswitch, maintained the temperature of the bath constant within plus or minus 1.5°C., a degree of control which was considered satisfactory for the polymerizations being studied. The 2000 watt unit was retained as an auxiliary heater to bring the bath up to temperature quickly.

Two methods were used for the preparation of experimental rubbers. Most of the early work on polymerization was done by the emulsion method. However it became apparent as the work progressed, that, for the preparation of a wide variety of polymers in appreciable quantities, emulsion polymerizations suffered from several important disadvantages.

A recipe which produced a satisfactory emulsion for one combination of monomers would precoatulate when another combination of monomers was tried. To obtain satisfactory emulsions of all the rubbers would have necessitated developing a different recipe and procedure for each of a large number of polymerizations.

Another drawback of the emulsion method involved the coagulation and washing of the polymers. It proved extremely difficult to coagulate the emulsions in the form of a crumb which could be adequately washed and dried. Without rapid stirring, the product precipitated as a lump which then had to be sliced for drying and washing; when this happened it was very difficult to isolate a pure rubber.

Since the emulsion technique involved too much variation and too much handling time, the bulk method of polymerization was investigated. The method which proved to be the most convenient and reliable was polymerization in 8 oz. tin cans.

The monomers used were either washed and dried, or fractionally distilled to remove inhibitor. In cases where the boiling point of the monomer was very high and fractionation was necessary for purification, the monomer had to be washed after fractionation to remove hydroquinone which had distilled over with the monomer. Seventy-eight rubber samples were polymerized by the above methods. These rubbers were largely copolymers of various alkoxy acrylates and methacrylates although some terpolymers were also made. The particular monomers were chosen because it was hoped they would confer improved heat stability and oil resistance.

The following monomers were used in various combinations with acrylamide and acrylonitrile: butyl acrylate, ethyl acrylate, methoxyethyl acrylate, butoxyethyl acrylate, 2-ethylhexoxyethyl acrylate, vinyl butyrate, vinyl butyl ether, and vinyl chloroethyl ether. Several copolymers of the same composition as American Monomers Acrylon rubbers were prepared for purposes of comparison.

The rubbers obtained for these bulk polymerizations contained perceptible amounts of monomer. To remove as much residual monomer as possible, the samples were milled into rough sheets.

The various rubbers were molded into 2 x 3 in. sheets on a Carver press. The specimens so obtained were tested for weight loss at 212°F. and at 350°F., and for solvent resistance at room temperature in a solution of 30% toluene 70% iso-octane and in water. The results are given in Table IV.

A few negative values appear in the % weight gain and % volume increase columns of Table IV. No great significance should be attributed to these values since the precision of the weighings with respect to the size of the samples was not great enough to justify any conclusions on the basis of variations of 1 or 2%.

Of the twenty-seven copolymers listed in Table IV, there are no figures given for seven samples in the columns for weight gain and for volume increase in the toluene-i-octane mixture. Of the seven, four are formulations corresponding to the Acrylon rubbers in monomer composition. The absence of figures for the hydrocarbon solvent test in the case of these seven rubbers is due to the deterioration of the test samples in the solvent to the point where they could not be handled for measurement at the end of the test period.

In evaluating the results of the tests it must be emphasized that the tests were carried out on uncompounded, uncured specimens. The same rubbers after reinforcement with carbon black or other agents, and cross-linking with curing agents would certainly be much less affected by solvents and probably would suffer less weight loss in the heat tests.

The Acrylon rubbers have already been found to have excellent oil resistance in the compounded and cured state. Since it may be expected that the properties of the raw rubbers will parallel those of the cured and compounded materials, it may be safely concluded that some of the rubbers reported should have extremely good resistance to solvents after compounding and curing, since under comparable conditions they are far superior to the Acrylons in this respect.

In general, it may be concluded that any copolymer for which figures are given in the test for hydrocarbon resistance is superior to the Acrylon rubbers in this respect. All the rubbers which fall in this category, with the exception of three, contain either acrylamide, or acrylamide and acrylonitrile in addition to an acrylate ester. From the results in the Table, it is evident that, of the modifications of the Acrylon formula investigated, the most successful was the inclusion of acrylamide.

The three copolymers nos. 56, 57, and 68, which show some superiority to the Acrylons though they do not contain acrylamide, in two cases include an acrylate containing an ether linkage. The third case includes vinyl butyrate. These results would require further investigation to establish whether the effect of these monomers is sufficiently favorable, especially in the case of the vinyl butyrate where only one successful example is available.

In summary, it may be said that the copolymerizations described point the way for the development of a rubber which would be a great improvement over the Acrylons.

Samples of the polymers were analyzed to check for changes in composition during polymerization. Calculation of the percentage of monomer is, of course, practical only in those cases where a single nitrogen containing constituent is present. For copolymers containing both acrylamide and acrylonitrile, it was not possible to establish the final composition by analysis for nitrogen. Therefore, Table IV only gives the actual analytical results.

Two 5 gram samples of copolymers of trifluoroethyl acrylate with

acrylonitrile were prepared in sealed test tubes and sent to the Wright Air Development Center for evaluation. Preliminary evaluation of these fluoro rubbers showed that considerable resistance to solvents was obtainable.

The physical properties of the compounded stock could not be too closely evaluated because the sample was scorched on curing.

In Table IV, the following abbreviations are used.

EA	--	Ethyl Acrylate
BA	--	Butyl Acrylate
AN	--	Acrylonitrile
MEA	--	2-Methoxyethyl Acrylate
BEA	--	2-Butoxyethyl Acrylate
EHEA	--	2-(2-Ethylhexoxy) ethyl Acrylate

TABLE IV

Preliminary Evaluation of Experimental Polymers

Run No.	Monomer	Compositor		% Wt. Loss (70 hrs/212°F.)	% Wt. Loss (24 hrs/350°F.)	% Wt. Loss 72 hrs/350°F.	% Wt. Gain 7 days 30% PhMe 70I-octane	% Vol. Gain 7 days, 30% Ph-Me 70I-octane	% Wt. Gain, 7 days in H ₂ O	% Vol. Gain 7 days in H ₂ O	% N Calcd.	% N Found
44	90 EA	10 AN	—	3.1%	2.4%	2.8%	—	—	0.9%	4.0%	2.6	2.7
45	90 EA	10 AN	—	1.8	1.9	3.3	—	—	2.1	6.3	---	---
46	90 EA	5 AN	5 AA	3.0	2.2	5.4	22.3	31.9	3.6	3.5	3.0	2.3
47	90 EA	5 AN	5 AA	3.4	2.2	3.2	22.7	32.5	5.4	6.3	3.0	2.6
48	85 BA	12 AN	3 AA	2.2	3.1	4.0	59.6	87.3	0	0	3.8	3.9
50	80 BA	20 AN	—	1.9	1.6	2.8	—	—	0.4	3.5	5.3	5.2
51	88 BA	12 AN	—	1.7	2.2	3.8	—	—	2.7	6.5	3.2	3.1
52	95 EA	5 AA	—	2.3	3.7	4.9	25.6	49.6	4.6	5.6	1.0	1.1
53	80 BA	15 AN	5 AA	2.9	3.8	5.1	44.0	63.0	1.0	1.3	5.0	5.1
54	80 MEA	15 AN	5 AA	3.7	3.4	5.1	-0.4	66.0	18.0	24.8	5.0	4.9
55	40 BA	40 MEA	20 AN	2.8	2.8	4.7	—	—	5.2	6.8	5.3	5.0
56	50 BA	30 BEA	20 AN	3.9	2.4	3.6	39.6	51.8	0.3	1.5	5.3	4.9
57	60 BA	20 EHEA	20 AN	6.3	2.7	4.0	58.0	77.8	-0.8	-1.9	5.3	4.7
58	40 BA	40 EHEA	20 AN	5.6	3.0	6.2	—	—	-2.0	-3.9	5.3	4.7
59	95 EA	5 AA	—	3.3	3.0	4.2	31.3	37.3	2.7	4.4	1.0	1.3
60	92.5 EA	7.5 AA	—	3.8	2.9	4.6	23.1	32.3	6.7	9.9	1.5	1.8
61	90 EA	10 AA	—	3.9	2.6	5.9	23.6	32.1	8.1	7.8	2.0	2.2
62	85 EA	7.5 AN	7.5 AA	4.6	2.7	4.2	57.6	66.8	4.2	6.2	3.5	4.1
63	70 BA	25 AN	5 AA	8.3	1.6	7.8	22.4	30.7	1.4	2.0	7.6	7.9
64	60 BA	25 AN	15 AA	1.4	2.0	4.5	3.6	31.8	1.3	15.1	9.6	9.8
65	95 EA	5 AA	—	1.2	1.9	2.7	17.3	33.9	0.5	1.3	1.0	1.0
67	11.4 AN	11.4 AA	77.2 EA	1.8	8.8	11.3	28.3	35.0	16.3	18.6	5.3	5.8
68	45 EA	45 VB	10 AN	5.6	0.9	1.5	19.2	37.6	-0.1	-1.9	2.6	4.2
69	45 EA	45 VB	10 AA	1.8	3.5	9.1	7.8	0.4	16.8	19.3	2.0	2.8
70	63.1 EA	26.4 VB	10.5 AN	3.9	1.3	2.5	—	—	1.2	1.4	2.8	3.3
71	12.5 AN	12.5 AA	75 EA	1.6	3.5	6.4	0.8	20.3	12.3	10.5	5.8	6.3
72	45 EA	45 VB	10 AA	3.8	2.8	4.5	29.3	43.3	11.6	13.4	2.6	2.1

EXPERIMENTAL

I. Vinylsilanes

A. Triallylvinylsilane

Run 1:

The materials used in this preparation were commercially available. They were fractionally distilled through a six foot column. A very narrow boiling point fraction of each material was taken. In the distillation of the trichlorovinylsilane, care was taken to exclude all possible traces of moisture. The ether was dried over sodium and distilled.

In a 3-l., three-necked flask equipped with stirrer, dropping funnel, and reflux condenser was placed 900 ml. of absolute ether and 40 g. of magnesium turnings. Allyl chloride (114 grams) was added dropwise.

A vigorous reaction soon took place with subsequent refluxing of the ether. Addition was continued at such a rate that gentle refluxing was maintained without any additional external heat. After about one-fourth of the allyl chloride had been added, the ether solution began to cloud up and on continued addition a white solid separated. Towards the end of the addition, a heavy white sludge was present. This was then stirred and heated to reflux for an additional hour.

The mixture was then cooled and 80 g. of trichlorovinylsilane dissolved in 600 ml. of ether was slowly added. A vigorous reaction resulted and external cooling of the reaction was necessary. The mixture was then heated to reflux for an additional three hours.

After decomposing this mixture by pouring into 4-l. of 10% sulfuric acid in ice water, the ether layer was separated and dried over anhydrous sodium sulfate. Fractional distillation of the dried ethereal solution yielded only ether, boiling point $34-36^{\circ}\text{C}$., and a second main fraction boiling point $49-51^{\circ}\text{C}/2\text{ mm.}$; n_D^{23} 1.4775; $D_{20}^{20} = 0.8313$. The yield was 23.5 g. or 28.2% of the theoretical.

In other runs, where the amount of ether used was less than above, the yield fell to 19%.

The materials also boiled at $65-66^{\circ}\text{C}/7\text{ mm.}$ When treated with

potassium permanganate in acetone or bromine in carbon tetrachloride, a definite positive test for unsaturation was noticed. The material is readily soluble in acetone, methanol, chlorinated solvents and aromatic solvents.

Run 2:

The following procedure gave a higher yield of triallylvinylsilane.

A 5-l. three-necked flask was equipped with a mercury-sealed stirrer, dropping funnel, and reflux condenser. The apparatus was protected from atmospheric moisture by the use of a calcium chloride drying tube. In the flask was placed 2500 ml. of absolute ether (dried over sodium and distilled) and 50 g. of magnesium turnings. While the contents were vigorously stirred, 145 g. of distilled allyl chloride was slowly added. A slight amount of refluxing occurred and a white solid mass separated. The mixture was fluid enough so that adequate stirring could be maintained while cooling with an ice-bath. To the white slurry was added slowly a solution containing 107 g. (87 ml.) of trichlorovinylsilane and 1200 ml. of absolute ether. An immediate reaction took place and gentle refluxing occurred. The addition of trichlorovinylsilane was controlled so that gentle refluxing was maintained while the flask was kept in the ice-bath.

The mixture was then refluxed for sixteen hours. After this reflux period, the reaction mass was cooled and decomposed by pouring it slowly into a mixture of 450 g. of concentrated sulphuric acid and 4000 g. of ice. The ether layer was separated and the aqueous layer extracted once with ether. The combined ether extracts were dried over anhydrous calcium chloride.

After removing the ether at atmospheric pressure, the residue was distilled under vacuum. The triallylvinylsilane was collected at 20 45-50°C/2-3 mm.. The yield was 40.1 g. or 37.5% of the theoretical. n_D^{20} 1.4782.

Using less ether or shorter reflux periods consistently gave lower yields. Filtering the reaction mixture free of magnesium salts and distilling the ether filtrate without hydrolyzing in sulfuric acid also gave lower yields. Analysis. Calcd. for $C_{11}H_{18}Si$: C, 74.2; H, 10.2. Found: C, 71.8; 71.7; H, 10.2; 10.2. On a triply fractionated product the analysis was as follows: Found: C, 71.13; 71.22; H, 9.91; 9.81.

Polymerization of Triallylvinylsilane:

One percent of benzoyl peroxide was dissolved in the monomer. It

was heated at 100°C for 24 hours with no signs of polymerization. The concentration of peroxide was raised to 5% and heated for 36 hours at 80°C. Still no signs of polymerization were observed.

The polymerization of a 3:1 ratio of styrene to triallylvinylsilane was initiated by 0.1% of benzoyl peroxide 100°C. After 15 hours a soft gel was produced. On continued heating, a hard, infusible polymer was formed.

Attempts to Make derivatives of Triallylvinylsilane:

Treatment with excess bromine-carbon tetrachloride solution and subsequent evaporation of solution under vacuum only produced a viscous oil which failed to crystallize.

Oxidation with excess potassium permanganate produced a water clear solution. On acidification of the clear filtrate no solid tetracarboxylic acid separated. The solution was extracted with various solvents but nothing was obtained.

B. Triphenylvinylsilane

Run 1:

Bromobenzene (240 grams) was treated in a Grignard reaction with trichlorovinylsilane. From the product residue there was obtained about 10 grams of a liquid, B.P. 85-95°C/3 mm., which crystallized on standing, m.p. 65-66°C.

This solid readily decolorized potassium permanganate and bromine solution. A mixed melting point determination with diphenyl, which melts at same temperature, was 50-60°C indicating that materials are not the same.

No better results in the preparation were obtained when benzene was added to the reaction mixture and the ether slowly distilled until a head temperature of 75°C was maintained for 24 hours.

Run 2:

In this case, the Grignard solution obtained from 400 ml. of ether, 40 g. of magnesium turnings, and 240 g. of bromobenzene was cooled and rapidly

poured through a glass wool plug directly into a dropping funnel. This filtered solution was added slowly to a stirred solution of 80 g. of vinyltrichlorosilane and 400 ml. of absolute ether. The mixture was refluxed for 15 hours and was decomposed by pouring into an excess of dilute sulfuric acid. The product was worked up in the usual manner, the final product was distilled:

Fraction	B.P., °C/3mm.	Remarks
I	95-110	12.5 g. identified as biphenyl by melting point and by mixed melting point with known material.
II	120-160	60 ml. of an oil which was unidentified.
III	160-185	10 g. of solid material. m.p. 65-66°C.
IV	Residue	10 g. red, oily material.

Fraction III. was the triphenylvinylsilane.
 Analysis. Calcd. for $C_{20}H_{18}Si$: C, 83.87; H, 6.34.
 Found: C, 84.0; H, 6.40.

C. Trimethylvinylsilane:

Absolute ether (500 ml.) was placed in a typical Grignard set-up and to it was added 40 g. of magnesium turnings. To this was slowly added 213 g. of methyl iodide. After the addition was complete, 80 g. of trichlorovinylsilane was slowly added. A vigorous reaction occurred and external cooling was necessary to control the reaction.

After treating the ethereal solution with aqueous sulfuric acid and fractionating, a small amount of liquid distilling at 40°C. was obtained. This gave positive permanganate and bromine tests for unsaturation.

D. Trimethallylvinylsilane:

Methallyl chloride was treated in a manner similar to that described for allyl chloride. After working up the ether layer, a larger fraction of oil remained which distilled at 113-114°C ; n_D^{18} 1.4235. This was identified as 2,5-dimethylhexadiene-1,5. From 174 g. of methallyl chloride there was obtained 70 g. of this hexadiene, which represents a yield of 70%. A residue remained which suddenly and violently polymerized. The use of magnesium powder in place of magnesium turnings gave no improvement in the reaction.

E. Tri-tert.-butylvinylsilane:

The preparation of tri-tert.-butylvinylsilane by the Grignard reaction of tert.-butyl magnesium bromide with trichlorovinylsilane in ether failed. A residue which was polymeric in nature was isolated.

F. Tricyanovinylsilane:

Attempts were made to substitute three cyano groups for three chlorines in trichlorovinylsilane by using sodium cyanide in a benzene solution. Other attempts were made using triethylamine as a catalyst in the absence of solvent and with silver cyanide or cuprous cyanide substituted for sodium cyanide. In no case could evidence for reaction be found.

G. Tri-(tri-chloromethyl)-vinylsilane:

No product could be isolated from the interaction of tri-chloromethyl magnesium bromide with trichlorovinylsilane.

H. Tri-(ethyl carboxymethyl)-vinylsilane

Run 1:

Reaction of trichlorovinylsilane with ethyl bromacetate in the presence of zinc at or near the boiling point caused a strongly exothermic reaction from which no product could be isolated.

Run 2:

Addition of zinc to a trichlorovinylsilane - ethyl bromoacetate - benzene solution at elevated temperatures in the presence of a crystal of iodine as catalyst did not induce a reaction.

Run 3:

Substituting zinc amalgam in the above procedure and adding a small quantity of ether, gave evidence of a reaction, however the product could not be isolated.

II. Methylenesilanes

The preparation of Methylenesilanes was unsuccessful.

In the course of the effort to prepare compounds with this grouping, a variety of compounds were prepared which are described below.

- A. Dimethyl-(dichloromethyl)-chlorosilane
- Methyl-di(chloromethyl)-chlorosilane
- Dimethyl-(chloromethyl)-chlorosilane

Run 1:

The procedure followed was essentially that of Kriebel and Elliot (76).

Chlorine gas was passed through a sintered-glass gas-dispersion tube into 340 g. (3.14 moles) of trimethylchlorosilane (Dow-Corning purified grade) contained in a 1-l., three-necked flask. The flask was placed in an ice bath and was fitted with a Dry Ice-acetone condenser and mechanical stirrer. The whole apparatus was protected from atmospheric moisture. The exit of the Dry Ice condenser was connected with a gas trap to dissolve out the hydrogen chloride as fast as it was produced. The chlorine was passed in at a rapid rate so that gentle refluxing of the mixture was maintained. The chlorine condensed at the Dry Ice temperature while the hydrogen chloride passed out and was dissolved in the gas trap.

The reaction flask was illuminated with an eight watt, G.E. germicidal lamp as a source of ultra-violet light. The hydrogen chloride that was liberated and dissolved in the water of the gas trap was continuously titrated with standard caustic solution so as to follow the course of the reaction. The chlorination was interrupted when 90% of the theoretical amount of hydrogen chloride had been evolved.

The reaction mixture assumed a characteristic green chlorine color just as long as chlorine was being passed into the solution. When the chlorine supply was stopped, the color disappeared leaving a clear, colorless solution.

The reaction mixture was distilled through an 45 cm. vacuum-jacketed, helix-packed column with a total reflux, partial take-off head. The apparatus was protected from atmospheric moisture.

A few milliliters of very low boiling material was discarded and the following fractions were collected:

<u>Fraction</u>	<u>B.P., °C.</u>	<u>Wt., g.</u>	<u>B.P., °C., Lit. (76)</u>	<u>Compound</u>
I	56-60	103.6	56-60	Me_3SiCl
II	60-112	8.1		
III	112-117	199.4	115	$\text{Me}_2(\text{CH}_2\text{Cl})\text{SiCl}$
IV	117-145	13.3		
V	145-153	41.1	149	$\text{Me}_2(\text{CHCl}_2)\text{SiCl}$
VI	153-167	12.2		
VII	167-169	8.8	172	$\text{Me}(\text{CH}_2\text{Cl})_2\text{SiCl}$
Residue		<u>21.2</u>		
TOTAL		407.7		

Based on recovered starting material, Fraction III represents a yield of 67% of the theoretical.

The density of Fraction III was D_{25}^{25} 1.0842.

Run 2:

Chlorination of 1463 g. (13.5 moles) of trimethylchlorosilane with 936 g. of chlorine by essentially the same procedure afforded

<u>Fraction</u>	<u>B.P., °C.</u>	<u>Wt., g.</u>	<u>Compound</u>
I	53-59	413.0g.	$(\text{CH}_3)_3\text{SiCl}$
II	113.8-116	880.0g.	$\text{CH}_2\text{Cl}(\text{CH}_3)_2\text{SiCl}$
III	145.8-150.4	275.4	$\text{CHCl}_2(\text{CH}_3)_2\text{SiCl}$
IV	169-173	86.6	$\text{CH}_3(\text{CH}_2\text{Cl})_2\text{SiCl}$

d_{25}^{25} 1.0821 lit. B.P. 115°C

Chlorine analysis of Fraction II indicated:

	<u>% Titratable Cl</u>	<u>Mol.Wt.</u>
Calc'd	24.84	143.1
Found	24.78	142.5

B. Dimethyl-(chloromethyl)-methoxysilane

1. Dimethyl-(chloromethyl)-methoxysilane:

Methanol (250 cc.), dried by refluxing with magnesium methylate was distilled into a dropping funnel. The dropping funnel was fitted with a reflux condenser. Sodium metal (23 g., 1 g. atom) was gradually added to the methanol in the dropping funnel. After the sodium was completely dissolved, the sodium methylate solution was added during a period of one hour, with stirring, to 143 g. (one mole) of chloromethyldimethylchlorosilane in a three-necked flask which was cooled in an ice bath. Sodium chloride precipitated rapidly. After the reaction mixture stood over night, the mixture was refluxed for two hours.

Most of the methanol was removed by distillation through a 30 cm. vacuum-jacketed column packed with one-eighth inch glass helices and using a total reflux, partial take-off head. The residue was transferred to a 250 ml. flask and was separated from the sodium chloride as far as possible by decantation. The salt was washed with dry methanol. The methanol was again separated by distillation with practically all the methanol distilling at 64°C. The distillate (total of 340 ml.) was added to 200 ml. of ice water. A small layer of organic material slowly settled to the bottom. The organic layer was separated and washed three times with small portions of saturated sodium chloride solution, shaken with anhydrous sodium sulfate, and filtered through a small piece of absorbent cotton. The material weighed 3.65 grams. The methanol distillate probably was an azeotrope of chloromethyldimethylmethoxysilane and methanol. The residue left after removal of the methanol was fractionally distilled.

<u>Fraction</u>	<u>B.P., °C.</u>	<u>Wt., -g.</u>	<u>% Cl Found</u>
I	70 - 120	8.1	----
II	120 - 120.5	20.4	24.8
III	120.5 - 120.75	33.3	25.0
IV	120.75 - 121	21.4	25.4

The residue weighed 11.04 g.

Calc'd: $C_4H_{11}SiClO$; 25.57%Cl; Found (Fraction IV) 25.4% Cl.

Fractions II, III, and IV combined represent a 54% yield of dimethyl-(chloromethyl)-methoxysilane, $D_{25}^{25} 0.9781$.

In a smaller run, a 45% yield was obtained. In a larger run, by the efficient use of the methanol distillate, the yield of the total product could be increased to 67%.

2. Reaction with magnesium:

Treatment of dimethyl-(chloromethyl)-methoxysilane with magnesium in ether afforded, in addition to unreacted starting material, a small amount of a product, b.p. 105-110°C/43 mm., a material in the range of dimeric materials rather than that of dimethylmethylenesilane.

3. Reaction with Zinc:

Similar treatment with zinc dust in isopropanol showed some evidence for the interchange of isopropoxy for methoxy groups.

III. Allyl Sulfides

A. Allyl 2-Hydroxyethyl Sulfide

1. Preparation:

In a 12-l. flask, a sodium methylate solution was prepared by adding 1490 g. of sodium methylate to 6000 ml. of absolute methanol. With cooling and stirring, 2000 g. of allyl mercaptan was then added. The allyl mercaptan dissolved from the sodium mercaptide. Ethylene chlorohydrin (2200 grams) was then slowly added. The reaction was exothermic, and addition was controlled so that gentle refluxing was maintained. Sodium chloride separated out. The mixture was stirred for an additional 24 hours.

The sodium chloride was collected on a filter, washed with methanol and discarded. The alcoholic filtrates are combined and fractionally distilled. After the methanol had been removed at atmospheric pressures, the residue was vacuum distilled. The product which distilled at 78-79°C/5-6 mm. was collected. This amounted to 1600 grams or 49.5% of theory. $n_D^{25} = 1.4975$; $D_{25}^{25} = 1.0256$.

The allyl 2-hydroxyethyl sulfide was redistilled and constants determined on a mid-cut in the fractionation. This fractionation was conducted in an all-glass apparatus consisting of a 50 cm. silver-lined vacuum-jacketed column and a vacuum-adapted total condensation, partial take-off head. The fraction b.p. 56-58°C/1 mm. was collected. $n_D^{20} 1.5069$; $D_{25}^{25} 1.0269$. Analysis. Calc'd: for $C_5H_{10}OS$: C, 50.81; H, 8.53; S, 27.13. Found: C, 50.90; H, 8.60; S, 27.4; 27.6.

2. Preparation of Derivatives:

a. p-Nitrobenzoate ester:

The p-nitrobenzoate ester was prepared but it was a non-crystalline material. A phthalimidomethylene ether was prepared but no sharp melting point could be obtained.

b. alpha-Naphthyl Urethane:

The alpha-naphthyl urethane was prepared from the allyl 2-hydroxyethyl sulfide and alpha-naphthyl isocyanate. This was recrystallized from low

boiling petroleum ether.

m.p. 73-73.5°C. Analysis. Calc'd for $C_{16}H_{17}O_2NS$:

C, 66.87; H, 5.96; N, 4.88; S, 11.16.

Found: C, 67.00; H, 6.00; N, 4.90; S, 11.3.

B. Allyl Vinyl Sulfide

1. Allyl 2-Chloroethyl Sulfide:

Caution: This material is a potent vesicant, simulating mustard gas in activity. It must be handled with extreme care. All reactions were conducted in a well-ventilated hood. Rubber gloves were used with an added precaution of dipping the hands, before and after use, into a strong hypochlorite solution. The gloves, as well as residual reagents, were intermittently placed in the hypochlorite solution. All apparatus was decontaminated by placing in a hypochlorite bath for two days. A total of three runs were made with varying amounts of ingredients. The conditions of the preparation were essentially as follows:

In a 1-l. three-necked flask, equipped with reflux condenser, dropping funnel, and mercury-sealed stirrer, was placed 236 g. (2 moles) of allyl 2-hydroxyethyl sulfide. To this was added slowly 400 ml. of concentrated hydrochloric acid. The mixture was then heated to 100°C. for four hours. During the addition of the hydroxyethyl sulfide, a homogeneous solution resulted which slowly clouded up on heating and finally separated into two layers.

The reaction mixture was allowed to stand overnight to complete the separation of phases. The chloro-sulfide layer existed as the heavier phase and was readily separated. It was repeatedly dried with anhydrous calcium chloride and finally fractionally distilled through the 50 cm. vacuum-jacketed column with total reflux, partial take-off head. After a few milliliters had been collected, the boiling temperature became constant at 46-49°C/3 mm.. A clear colorless mobile liquid, having a mustard-like odor, was collected.

Yield in this case amounted to 119 g. or 43% of the theoretical.
 n_D^{20} 1.5067; D_4^{25} 1.0719. Literature (27) gives a value of b.p. 66-67°C/14 mm.;
 n_D^{20} 1.5071; D_4^{20} 1.0761.

A considerable amount of residue (74 g.) remained in the still pot. This was believed to be 2-chloroethyl-2-chloropropyl sulfide, prepared by the simultaneous addition of hydrogen chloride to the allyl double bond, as well as replacement of the hydroxyl group.

Lower concentration of hydrochloric acid than used above gave a lower yield of product as well as a lower yield of residue, which indicated incomplete reaction. Raising the temperature of reaction mixture to reflux gave more residue (dichloro derivative) and less product.

2. Allyl Vinyl Sulfide

a. Use of Quinoline:

To 421 g. (3.37 moles) of quinoline, heated to 140°C. in a reflux set up, was added 153 g. (1.26 moles) of allyl 2-chloroethyl sulfide was added. No rise in temperature of the reaction mixture was noticed. The temperature of the oil bath was raised slowly to 270°C. Practically no material distilled. A sulfide odor was detected in the distilling flask and a black tarry material remained in the still pot.

b. Use of Alcoholic Potassium Hydroxide:

The dehydrohalogenation procedure was essentially that described by Bales and Nicholson (27).

In a flask was placed 860 ml. of methanol, 214 ml. of water, and 252 g. of potassium hydroxide. The mixture was heated to reflux and with the heat removed, 147 g. of allyl 2-chloroethyl sulfide was added. Gentle refluxing maintained itself during the addition. Solid salt separated from the reaction mixture. Refluxing was continued for an additional one and one-half hours. The mixture was distilled and each 200 ml. sample of distillate was poured into 1600 ml. of water. Three such samples were collected, but in each instance no insoluble oil separated.

The residue was filtered free of salt and an attempt to fractionate it at reduced pressure was made. No product could be isolated.

The residue which remained was black and viscous and had a definite sulfide odor.

IV. Divinyl Sulfide

A. 2,2-Dichloroethyl Sulfide (Mustard Gas):

In a 5-l. three-necked flask, fitted with a dropping funnel, reflux condenser, and mercury sealed stirrer was placed 1780 ml. of concentrated hydrochloric acid. To the acid was slowly added 723 g. (5.9 moles) of 2,2'-dihydroxyethyl sulfide. The temperature of the reaction mixture rose to 44°C. Additional heat was applied until a temperature of 60-70°C was attained. The contents was kept at this temperature for two hours. The mixture was cooled and the heavy oil layer was separated. Weight of product was 430 grams.

B. Dehydrohalogenation:

The method used was that of Bales and Nicholson (27). Potassium hydroxide (564 g.), 480 ml. of water, and 1920 ml. of methanol were placed in a 5-l. three-necked flask. The mixture was stirred and brought to reflux. The external heat was discontinued and 430 g. of the dichloroethyl sulfide was added at such a rate that gentle refluxing was maintained. Salt separated from the reaction mixture. Refluxing was continued for an hour after the addition had been completed. The mixture was then distilled. Each 200 ml. of distillate was added to 1600 ml. of water and the oil layer that separated was collected. The distillate was collected in the above manner until no more oil separated on adding to water. Four such fractions were collected. The last gave no oil on treating with water. The oil layers from all the fractions were combined and dried over anhydrous sodium sulfate. The mixture was inhibited with hydroquinone and p-phenylenediamine. The dried product was then fractionally distilled. The fraction boiling at 84-85°C. was collected. The yield was 70 grams.

n_D^{20} 1.5065; $D_4^{29.4}$ 0.8985. Literature: b.p. 85-86°C ; D_4^{19} 0.9174.

The product was inhibited with 0.1% of hydroquinone and 0.1% p-phenylenediamine.

V. 2-(Methylthio)-ethyl Vinyl Sulfide

A. 2-Methylmercaptoethanol:

There was dissolved 5.78 kg. (107 moles) of sodium methylate in 24-l. of methanol contained in a 50-l. flask. While stirring with a centrifugal type glass stirrer sealed with a rubber sleeve, 6.12 kg. of methyl mercaptan was passed in through a stainless steel dispersion disc. (theoretical amount is 5.136 kg.). The outlet of the flask was connected to a 5-l. flask containing a solution of calcium hypochlorite, followed by a trap containing lead acetate.

The sodium methyl mercaptide solution was heated to reflux. Large amounts of excess methyl mercaptan were evolved. After the solution had reached the reflux temperature, 10.19 kg. (126.8 mole) of ethylenechlorohydrin (anhydrous) was added at such a rate that the solution boiled vigorously without external heating.

Upon cooling, the methanol solution was separated from sodium chloride. The solution distilled as follows:

Forerun:	up to 77°C/60 mm.	0.71 kg.
Product	77°C/60 mm. - 83°C/34 mm.	8.23 kg.

B. 2-Chloroethyl Methyl Sulfide:

To a solution of 4270 g. of methylmercaptoethanol in 3-l. of chloroform in a 12-l. three-necked flask fitted with an anchor-type glass stirrer, dropping funnel, and reflux condenser connected to a gas trap through a drying tube, 6.15 kg. of thionyl chloride was added slowly at a rate sufficient to maintain the solution at reflux temperature. The reaction mixture was allowed to stand overnight. The reflux condenser was then replaced with a fractionating column and still-head. Then the chloroform and excess thionyl chloride were distilled off. Large volumes of gas were evolved before the solvent started to distill. Only about one third of the solvent was recovered, the remainder had probably been carried off with the gases evolved during the reaction.

Distillation was continued under vacuum. The temperature reached 53°C/32 mm.. After 100-150 ml. had been collected, a main fraction of 4.06 kg., (81% yield; b.p. 53-7°C/32 mm., was obtained.

C. 2-(Methylthio)-ethyl 2'-Hydroxyethyl Sulfide:

To 1-l. of methanol in a 3-l. three-necked flask fitted with a mechanical stirrer and a reflux condenser protected with a Drierite drying tube, there was added in small portions 93 g. of sodium metal. After solution of the sodium was complete, 345 g. (4.4 moles) of 2-mercaptoethanol was introduced. Then 442 g. (4 moles) of 2-chloroethyl methyl sulfide was added at a rate sufficient to maintain the mixture at reflux without external heating. The mixture was allowed to stand overnight, heated under reflux 2 hours, cooled, and filtered. The sodium chloride was washed twice with methanol. The combined filtrate and washings were distilled through a column packed with glass helices. The distillation was conducted under a pressure of 42 mm.. When the vapor temperature at the still-head reached 70°C, the water pump was replaced by an oil pump. A small forerun was taken to 138°C/9 mm.. As the temperature approached 138°C., the color of the distillate changed from colorless to yellow. The main fraction was collected from 138°C/9 mm. to 145°C/12 mm.. Some cloudiness also appeared in the distillate. The product was clarified with charcoal which removed the cloudiness but not the color. The yield was 511.6 g. or 84% of the theoretical amount.

In a 3-l. three-necked flask fitted with a dropping funnel, reflux condenser, and mechanical stirrer, a solution of 216 g. (4 moles) of sodium methylate in 1-l. of methanol was prepared. To this solution was added 330 g. (4.23 moles) of freshly distilled mercaptoethanol b.p. 68-69°C/24 mm.. After this addition had been completed, there was then added 442 g. (4 moles) of 2-chloroethyl methyl sulfide at a fairly rapid rate.

The chloro-compound did not seem to react as rapidly as it was added, since fifteen minutes after the addition was complete, the reaction was vigorous enough to flood the reflux condenser.

After the reaction had subsided, the mixture was heated under reflux for three and one-half hours.

The work-up of the product was essentially as in the previous run. The pale yellow product was collected at 125-8°C/6 mm.. Its weight was 372.3 grams.

D. 2-(Methylthio)-ethyl Vinyl Sulfide

Run 1:

In a 5-l. three-necked flask fitted with an anchor-type glass stirrer, a reflux condenser which had been connected through a drying tube to a gas trap, and an addition funnel, there were dissolved 511 g. (3.36 moles) of 2-methylthioethyl 2'-hydroxyethyl sulfide in 750 ml. of chloroform. Over a one hour period, 275 ml. (3.85 moles) of a technical grade of thionyl chloride in 800 ml. of chloroform was added to the solution. As the addition progressed, the color of the solution changed from yellow to deep red.

After the addition had been completed, the solution was heated under reflux for three hours.

The bulk of the solvent was removed by distillation. The residue was heated under vacuum to remove the remaining solvent and dissolved gases.

A solution of 78 g. (3.39 moles) of sodium metal in 1-l. of methanol was prepared and added to the residue. A dark, tarry mass was precipitated by the addition of the sodium methylate solution. The supernatant solution was separated from the tar by filtration through a filter stick and by decantation. The tarry residue was washed with methanol. The combined filtrate and washings were concentrated by distilling off the methanol through a fractionating column. The distillation residue was transferred to a 1-l. three-necked flask fitted with a stirrer and a small column. On distillation under reduced pressure, decomposition took place with a volatile product collecting mostly in the Dry Ice trap. No product boiling at the boiling point of the desired product was isolated.

Run 2:

In a 300 ml. round-bottom flask equipped with a special sidearm, were placed 100 ml. of dry ether, 15.2 g. (.01 mole) of 2-methylthioethyl 2'-hydroxyethyl sulfide, and 0.5 ml. of pyridine. The flask was fitted with a reflux condenser connected through a drying tube filled with Drierite to a gas trap. A dropping funnel was attached to the sidearm and 13.1 g. (0.11 mole) of purified thionyl chloride (b.p. 77°) in 50 ml. of dry ether was added rapidly. A turbidity, which later separated as a small layer of oil, formed as the thionyl chloride was added. The ether solution remained practically colorless. The mixture was allowed to stand for two hours at room temperature; then it was heated under reflux for one hour.

The solvent was removed by evaporation at reduced pressure. The operation was carried out by connecting a water aspirator through a drying tube to the system, and by substituting a capillary tube connected to a balloon filled with dry nitrogen for the dropping funnel in the sidearm. The cooling from the evaporation of the ether resulted in the separation of the product as a white crystalline solid which later melted to a pale

yellow liquid as the flask was warmed by an oil bath. Goldsworthy, et al. (58) describe the hemi-mustard as melting at 7-13°C..

The material was left under reduced pressure over-night at 30-35° to remove traces of thionyl chloride and hydrogen chloride. The residue was dissolved in 30 ml. of methanol. Then, a solution of 3 g. (0.13 mole) of sodium in 50 ml. of methanol was added. The solution was heated under reflux overnight.

The supernatant liquid was decanted from the sodium chloride, which had precipitated, diluted with an equal volume of water, and extracted three times with petroleum ether. The petroleum ether solution was washed with saturated sodium chloride solution, shaken with anhydrous magnesium sulfate, and filtered. The solvent was removed by distillation through a micro-column at atmospheric pressure, and the distillation continued under reduced pressure. A colorless distillate of 10.05 grams, which turned pale yellow on standing, was obtained, boiling range 120-132°C/22 mm.. The product decolorized bromine in carbon tetrachloride rapidly.

A large scale preparation was then carried out as follows: In 1-l. of dry ether contained in a 5-l. three-necked flask was dissolved 197.5 g. (1.3 mole) of 2-methylthioethyl 2'-hydroxyethyl sulfide and 2 ml. of pyridine. The flask was fitted with an anchor-type glass stirrer, dropping funnel, and a reflux condenser connected through a drying tube to a gas trap. To this solution was added slowly, with stirring, a solution of 170.2 g. of thionyl chloride (purified) in 500 ml. of ether.

The reaction mixture became milky after 15-20 ml. of thionyl chloride solution had been added. The milkiness was superseded by the separation of a small, light brown layer at the bottom of the flask. After the addition had been completed, the pale yellow solution was heated under reflux for two hours. A distillation head was placed at the top of the reflux condenser, which was emptied of cooling water, and ether was removed. After almost all the ether had been distilled out, the system was evacuated with a water pump for four hours.

To the hemi-mustard in 150 ml. of methanol, a solution of 32. g. (1.39 mole) of sodium in 500 ml. of methanol was added over a one-half hour period. The mixture was heated, with stirring, under reflux for five hours. After cooling, the methanol solution was decanted from the sodium chloride into an equal volume of water. The residual sodium chloride was washed thoroughly with benzene. The product was extracted with benzene, the benzene solution was washed twice with a saturated sodium chloride solution, then the benzene solution was shaken with anhydrous magnesium sulfate.

After filtration into a one liter flask, the bulk of the benzene was removed by distillation through a small column packed with one-eighth inch glass helices, and fitted with a total reflux partial take-off head. The residue was transferred to a 300 ml. flask and, after addition of the 10 g. of material from the trial run described above, fractionally distilled. The following fractions were obtained:

<u>Fraction</u>	<u>B.P., °C/5 mm.</u>	<u>Wt., g.</u>
I	52-62°	55.7
II	62-82°	5.2
III	82-85°	108.6

The boiling point given by Brown and Moggridge (57) for 2-methylthioethyl vinyl sulfide is 65°/2 mm.. A sample of 100 g. of Fraction III was submitted. The infrared spectrum of this material, taken at Wright Air Development Center, indicated that this fraction contained no appreciable vinyl linkage.

Fraction I, which was the minor product, proved to be the desired product. It was again fractionated through a short column packed with 1/8" glass helices, as follows:

<u>Fraction</u>	<u>B.P., °C/14 mm.</u>	<u>Wt., g.</u>	<u>%C</u>	<u>%H</u>	<u>%S</u>	<u>n_D^{25}</u>
I A	to 84	3.1				
I B	84-6	24	44.5	7.5	47.7	1.5431
I C	86	23	44.7	7.5	47.4	1.5424
Calc'd for $C_5H_{10}S_2$			44.73	7.51	47.77	

The specific gravity of Fraction B using a 4 ml. pycnometer was found to be $D_{25}^{25} = 1.0427$.

It is impossible to reconcile a boiling point of 52-62°C/5 mm. or 84-6°C/14 mm. with a boiling point of 65°C/2 mm. as reported in the literature. The difference in the boiling point found by Brown and Moggridge and their failure to detect a second reaction product may be ascribed to the small quantity of material with which they worked. It must be noted that their vinyl compound was prepared by the dehydrohalogenation of only 10 g. of chloro-compound. They also used sodium ethylate instead of sodium methylate, which we used. They reported a value of sulfur which agrees well with the calculated value for the vinyl compound.

The major component of the isolated products from this preparation were shown to be 2-methylthioethyl 2'-methoxyethyl sulfide by analysis for carbon, hydrogen, and methoxyl; and by the infrared spectra prepared at the Wright Air Development Center.

VI. Vinylidene Cyanide

Run 1:

To a solution of 485 g. of malononitrile in 500 ml. of methanol was added 282 g. of a 37% formaldehyde solution followed by 2 ml. of piperidine. The solution was mixed while cooled in an ice bath. Crystallization of the product began after two hours in the ice bath. After the reaction mixture had stood in the cold for 20 hours, the product was collected on a filter. Washing the solid with one per cent. hydrochloric acid solution removed the color almost completely. The acid wash was followed by washing with cold water. The product (300 g.) melted at 138-142°C.

The product could be recrystallized from 2:1 acetonitrile--benzene.

A layer of glass wool sprinkled with phosphorus pentoxide was placed over 56 g. of tetracyanopropane in a 300 ml. flask. A distillation head delivering directly into a receiver containing phosphorus pentoxide and cooled in Dry Ice-acetone was connected to the flask. The system was evacuated to 1-2 mm. Hg. The flask was placed in an oil bath heated to 180°C. During 3-4 hours, the distillate which solidified continued to accumulate in the receiver. At the end of the distillation, the head and delivery tube into the receiver were almost completely clogged with crystalline solid. This was probably from recombination of malononitrile with vinylidene cyanide. The material in the receiver was distilled over phosphorus pentoxide through a one foot Vigreux column. The distillate weighed 9.07 g., boiling point 63-4°C/23 mm. A drop added to a few milliliters of water polymerized instantly. The receiver which contained phosphorus pentoxide was then sealed. An approximate melting point was obtained by freezing the material in a salt-ice mixture and then allowing it to warm slowly in a cold water bath contained in a double walled glass vessel. The temperature of the bath rose approximately 1°C in four minutes until the vinylidene cyanide started to melt at 8°C. The bath then warmed up to 12°C during a period of one hour at the end of which time the product had completely melted. Because of the lag between the bath temperature and the interior of the ampoule, the actual melting point is probably somewhat lower than 8-12°C. The melting point of a fractionally crystallized sample of vinylidene cyanide is given by Ardis as 9.7°C (60).

Run 2:

A solution of 200 g. of malononitrile and 110 g. of 37% formaldehyde solution in 300 ml. methanol was cooled in ice. To the cold solution was added 12 drops of piperidine. The solution was seeded with tetracyanopropane and allowed to stand in a cold place. Approximately 100 hrs. after mixing, the product was collected and washed with dilute hydrochloric acid (1-2%). The white product (thin plates) melted completely at 136-41°C. The yield of tetracyanopropane was 175 grams. The product was dissolved in 125 ml. of

ket acetonitrile to which a trace of phosphorus pentoxide had been added. The acetonitrile was diluted with 80 ml. of benzene. After most of the product had crystallized, the flask was cooled in ice. The product was collected and washed with a 1:1 benzene-acetonitrile mixture. The product weighed 146.5 g., m.p. 137-9°C after softening at 132°C. Diels *et al* (61) obtained 1.5 g. of crude tetracyanopropane from 4 g. of malononitrile.

For the second preparation of vinylidene cyanide, the same apparatus was used as in the previous run. A total of 129 g. of tetracyanopropane including 17 grams recovered from the first run was processed. The rest of the distillation apparatus, including the receiver, was sprinkled with phosphorus pentoxide. The apparatus was evacuated to 2 mm. and the receiver and trap cooled in a Dry-Ice-acetone mixture. The still pot was heated in an oil bath maintained at 170-80°C. Heating was discontinued after eight hours and dry air was admitted to the system. The distillate collected weighed 49 grams. About 1 milliliter had collected in the Dry Ice trap. A heavy solid cake was left in the still pot and in the neck of the flask.

The third preparation was carried out in the same manner using 107 g. of tetracyanopropane, m.p. 137-9°C. The product that was collected weighed 70 grams.

The combined products, 127 g., were fractionated through a one foot Vigreux column with a total reflux, partial take-off head under reduced pressure. A forerun of a few drops was discarded. The fraction b.p. 47-48°C/9 mm., was taken as the main product. This weighed 61 grams. An intermediate fraction of 5.5 g. was distilled up to 80°C followed by malononitrile (42 g.) which distilled almost entirely at 96-7°/9.5 mm.

The vinylidene cyanide was frozen and allowed to melt slowly while shaking with a thermometer immersed in the liquid. The melting point range was 9.1-10.5°C. Ardis, *et al* (60) described a sample purified by several recrystallizations as melting at 9.7°C. The product which was stored over a small amount of phosphorus pentoxide in a sealed ampoule turned a faint yellow on standing.

VII. N-(2,2,2-Trifluoroethyl)-acrylamide

A. Trifluoroacetamide:

In 300 ml. of absolute ether was dissolved 640 g. (5 moles) of methyl trifluoroacetate and 105.5 g. (6.2 moles) of ammonia gas. After evaporation there was obtained 525 g. or 90% of the theoretical of trifluoroacetamide. Melting point 75-77°C; Literature (77) melting point 75°C.

B. Trifluoroethylamine:

Caution: The lithium aluminum hydride used in this preparation was obtained from Metal Hydrides, Inc. of Beverly, Massachusetts. It is packed in tin cans containing large pieces of the hydride. This is ground in the can, using a pestle, and transferred on aluminum foil to the reaction flask. A nitrogen flow of between 3-4 cu. ft./hour was continually passed through the system. Extreme caution was exercised so that no water or moisture would come in contact with the hydride or hydride solution until after completion of the reaction. The water, that was used at the end of the reaction to decompose any excess hydride, was added through a tube that was just over the surface of the solution. The tube was so placed that none of the water would hit the walls of the flask where residual hydride might have dried out.

The reaction was conducted in a 12 liter three-necked flask fitted with a mercury-sealed stirrer, dropping funnel, nitrogen gas inlet tube, and a reflux condenser which was protected from atmospheric moisture by a calcium chloride tube.

Four liters of absolute ether was placed in the flask. A steady stream of nitrogen gas was passed through the system. Crushed, but not ground, lithium aluminum hydride (203 g., 5.3 moles) was added portion-wise to the ether over a period of 2 hours. A slight amount of exotherming accompanied the addition of the lithium aluminum hydride. To the hydride solution was slowly added, in a dropwise manner, a solution containing 543 g. (4.8 moles) of trifluoroacetamide in 1-l. of absolute ether. The reaction exothermed during the course of the addition. About 3 hours were required for the addition. An additional liter of absolute ether was added to the reaction flask at the end of the addition to restore the volume of the ether which had been lost due to entrainment. The reaction mixture was stirred an additional 12 hours.

The excess lithium aluminum hydride was deactivated by cautiously adding 185 ml. of water dropwise. The exit of the condenser was placed in a dilute sulfuric acid bath to trap any amine that might escape due to entrainment. A solution containing 1290 ml. of concentrated sulfuric acid and 3000 g. of ice was then added to the reaction mixture. When half of the acid had been added, the reaction mixture became thick, but thinned out when the addition was completed.

The resulting reaction mixture was a two-phase liquid system containing suspended solid. The clear, supernatant liquids were decanted and the residue was filtered and washed well with 700 ml. of ether. The solid was saved for subsequent treatment. The decanted liquids, filtrate, and wash solution were combined and separated. The water phase was extracted twice with 200 ml. portions of ether. The water layer was saved.

The wet, solid material (2100 g.) was placed in a 5-l. three-necked flask which was fitted with a mechanical stirrer and distillation set-up. The distillation receiver was connected, in turn, to a cold trap. Both the receiver and cold trap were immersed in an alcohol, salt-ice bath. A solution of 1720 g. of sodium hydroxide in 2300 g. of water was added to the solid over a period of one hour. The reaction was very exothermic and was moderated by placing the flask in an ice bath. The resulting mixture was a thick slurry. After all of the solid had become suspended, the reaction mixture was distilled. Distillation was continued until a vapor temperature of 100°C was reached. A total of 52 g. of amine odored distillate was collected.

The water layer which was previously saved from the original filtration was slowly added to 1700 g. of solid sodium hydroxide which was contained in a 12-liter, three-necked flask. The flask was contained in an ice bath and was fitted with reflux condenser, stirrer, and distillation set-up. The addition required 2.5 hours. The mixture was distilled and the distillate collected from 36°-100°C.

The distillates from both neutralizations were combined. Sodium hydroxide (50 g.) was added to dry the mixture which was then fractionally distilled through a 50 cm. helix-packed column with a total reflux, partial take-off head. The trifluoroethylamine was collected at 34-36°C. Literature (74): b.p. 37-37.5°C. The yield was 182 g. or 38% of the theoretical. The trifluoroethylamine was found to be extremely volatile at room temperature.

C. N-(2,2,2-Trifluoroethyl)-acrylamide:

The reaction was carried out in a 3-l., three-necked flask which had been fitted with a mercury-sealed stirrer, dropping funnel and reflux condenser which was protected from atmospheric moisture by a calcium chloride drying tube. Into the flask was charged 182 g. (1.84 moles) of 2,2,2-trifluoroethylamine and 1700 ml. of absolute ether. The flask was placed in an ice bath. The solution was stirred and 83.3 g. (0.92 moles) of redistilled acrylyl chloride was added dropwise. The addition required one-half hour. The reaction was exothermic with accompanied deposition of white solid trifluoroethylamine hydrochloride. The reaction mixture was stirred for one hour after the addition had been completed.

The resulting suspension was filtered free of solid. The solid was washed with three 50 ml.-portions of ether. The air-dried 2,2,2-trichloroethylamine hydrochloride weighed 117 grams.

A solid remained after the filtrate was evaporated to dryness at room temperature and at reduced pressures. This solid had a tendency to melt when the room temperature had become slightly higher than normal. This was caused by residual traces of ether present in the solid. In this molten state the material polymerized to a considerable degree.

The dried solid melted in the range of 70-75°C. The crude yield was 133 grams.

The product was slightly soluble in cold petroleum ether but fairly soluble in the hot. It was completely soluble in ether, methanol, and benzene.

The crude product was recrystallized from 5-l. of boiling petroleum ether. The clear, supernatant, hot solution was decanted from undissolved solid material. The residue was extracted with two 500 ml. portions of boiling petroleum ether. The combined hot solutions were cooled to 19°C. The crystals which formed were collected on a filter and washed with three small portions of petroleum ether.

The melting point of the recrystallized material was 74.5°-76°C. The yield was 64 g. or 45.7% of the theoretical.

A small portion (1 g.) of the product was recrystallized from 60 ml. of petroleum ether to which had been added a trace of carbon black. This sample was dried under vacuum at room temperature. Melting point was 74.5°-75°C.

Analysis Calc. for $C_5H_6ONF_3$: C, 39.22; H, 3.95; N, 9.15

Found: C, 39.00; H, 4.10; N, 9.00.

VIII. 1,1-Dihydroheptafluoro-1-butyl alpha-(Trifluoromethyl)-acrylate

A. Methyl Perfluorobutyrate:

Perfluorobutyric acid was esterified by standard methods with methanol in yields varying between 95 and 97.4%. Physical constants: b.p. 79-81°C, n_D^{20} 1.293; D_{25}^{25} 1.4773.

B. Methyl Perfluoroacetate:

Perfluoroacetic acid was esterified by standard procedure with methanol. Yields varied between 59 and 85%. Physical constants; b.p. 43-44°C; n_D^{20} 1.290; D_{25}^{25} 1.2744.

C. 1,1-Dihydroheptafluoro-1-butanol:

In a 5-l. three-necked flask fitted with a condenser topped by a drying tube, a stirrer, and a gas-inlet tube through which the system was filled with nitrogen, 50 g. (1.32 moles) of lithium aluminum hydride was dissolved in 1-l. of anhydrous ether. Then the apparatus was placed in an ice bath.

Over a three-quarter of an hour period, a solution of 570 g. (2.5 moles) of methyl perfluorobutyrate in 1-l. of ether was added at such a rate that reflux was maintained despite the ice bath.

The mixture was allowed to warm to room temperature, and was maintained at that temperature for 12 hours.

Then 25 ml. of water was added. This was followed by a solution of 240 ml. of concentrated sulfuric acid in 600 ml. of water.

The ether layer was separated, the aqueous mixture was extracted with fresh ether and the ether layers combined. Then the ether solutions were dried with Drierite.

After removal of the ether, the residue was fractionally distilled. The fraction with boiling range of 76-97°C was preserved. This fraction was refluxed with 105 ml. of concentrated sulfuric acid and then fractionally distilled. The desired alcohol was the main product isolated at

96-97°C/757 mm., n_D^{20} 1.2995, d_{25} 1.576 g./ml. (literature: 95°C/749 mm. (77)).
Weight 257.3 g. (51% of theory).

D. Methyl alpha-(Trifluoromethyl)-acrylate:

Before attempting the preparation of methyl alpha-(trifluoro-methyl)-acrylate from trifluoroacetone cyanohydrin, several model reactions were run with acetone cyanohydrin to determine proper reaction conditions.

To 6.4 g. of methanol, there was added, with cooling and shaking, 21 g. (11.2 ml.) of conc. sulfuric acid, followed by 13.9 g. (0.1 mole) trifluoroacetone cyanohydrin. The flask was heated for 1 hour in an oil bath at 100-105°C. The bath temperature was then raised to gentle reflux at 135-140°C and maintained thus for 1 hour. The solution became cloudy. Water (4 ml.) was added to the mixture which was then heated under reflux for 12 hours.

On standing, a crystalline mass separated from solution, water was added to dissolve the solid. The organic layer (bottom layer), which had a pleasant ester-type odor, was separated and washed with 5% sodium bicarbonate solution. The evolution of gas during this step caused a small amount of product to be lost. After washing with water followed by saturated sodium chloride solution, the product was distilled through a micro column. A main fraction of 7.02 grams, n_D^{25} 1.3565, distilled at 127-8°C.

The molecular weight of the product boiling between 127-8°C was found to be 175 by saponification with alcoholic alkali as compared with a calculated value of 154 for methyl alpha-(trifluoromethyl)-acrylate ($C_5H_5F_3O_2$) and of 172 for methyl alpha-hydroxy-alpha-(trifluoromethyl) propionate ($C_5H_7F_3O_3$). The following values were obtained on analysis for carbon and hydrogen:

	% C	% H
Found	34.59	4.65
Calc'd for $C_5H_5F_3O_2$	38.97	3.27
Calc'd for $C_5H_7F_3O_3$	34.89	4.10

Darrall, et al (78) have prepared methyl alpha-hydroxy-alpha-(trifluoromethyl)-propionate by esterifying the corresponding hydroxy acid. They describe it as boiling at 127-9°C, n_D^{14} 1.358.

Since adding the methanol to the sulfuric acid before adding the cyanohydrin introduced some water, a second run was made using the standard procedure for the preparation of methyl methacrylate.

To 13.9 g. (0.1 mole) of trifluoroacetone cyanohydrin, there was added slowly with shaking 7.6 ml. (14 g.) of conc. sulfuric acid. Practically no heat was evolved during the addition, but a few minutes after all the cyanohydrin had been added, a vigorous reaction, which was moderated by cooling in cold water, began. The mixture frothed and became progressively more viscous. The top temperature was held down to 90°C.

After the reaction subsided, the flask was heated in an oil bath at 125-135°C for half an hour. The mixture was cooled to 70°C and 7.5 ml. of methanol was added to it with shaking. The mixture was allowed to stand for 3 hours, and was then heated at 90-100°C for 2 hours. There was then added 2 ml. of water, and the resulting mixture was heated under reflux for 3 hours. On standing overnight, a crystalline solid separated. Water was added to dissolve the solid and the bottom layer was separated. The organic material was washed twice with 5% sodium bicarbonate solution, once with water, and once with saturated sodium chloride solution. After filtering through a bed of anhydrous magnesium sulfate, the solution was fractionally distilled.

Fraction	B.P., °C	Wt. g.	n_D^{25}
I	92-126	1.21 (wet)	
II	126-30	5.8	1.3569
III	130	1	1.3565

The product apparently was the same as that obtained in the first preparation.

The results obtained are not in harmony with the preparation using methyl hydrogen sulfate described in U. S. Pat. 2,541,465. No physical constants were given for the compound in that patent.

IX. 1,3-Dicyano-1,3-butadiene

A. 1,3-Dichloro-2-propanol:

By conventional methods, 1091.5 g. (12.4 moles) of epichlorohydrin was hydrolyzed at ice-temperatures with 1200 ml. of concentrated hydrochloric acid. Repeated fractional distillation of the product gave 1284.2 g. of 1,3-dichloro-2-propanol, b.p. 70°C/13 mm (160-162° C/at. press.), an 84.5% yield.

B. 1,3-Dicyano-2-propanol

Several attempts were made in this laboratory to prepare 1,3-dicyano-2-propanol from the corresponding dichloro compound.

Run 1:

A water solution of 2 moles of commercial sodium cyanide was added dropwise to a methanol solution of 1 mole of 1,3-dichloro-2-propanol. A gentle reflux was maintained by regulation of the rate of addition.

The exothermic nature and the color changes were considered evidence of reaction.

Water and methanol were removed by distillation at reduced pressure. The residue was extracted with boiling ethyl acetate. After distillation of the ethyl acetate extract the dark viscous oily residue proved very difficult to distill even at 200°C/10 mm.

In subsequent attempts similar procedures were used.

Run 2:

A methanol solution of sodium cyanide was added to the methanol solution of 1,3-dichloro-2-propanol. After following the previous product isolation procedure, the residue was treated with an excess of P_2O_5 at approximately 240°C and at 1 mm. of pressure. No isolatable quantities of 1,3-dicyano-1-propene were found.

Run 3:

To a water solution of 3 moles of sodium cyanide, 1 mole of 1,3-dichloro-2-propanol was added. After an induction period, ice baths were required to maintain a reasonable rate of reflux.

The product extract was dried over sodium sulfate. Attempts to dehydrate the product with potassium acid sulfate, at reduced pressure and high temperature were not successful.

Run 4:

A preparative attempt using cuprous cyanide in a methanol medium also failed to afford a tangible amount of product.

C. 1,3-Dichloro-2-propyl Acetate:

Several different procedures for the acetylation of 1,3-dichloro-2-propanol have been used at this Laboratory. Although a rather large portion of high boiling by product was formed in the preparation detailed below, this procedure was found to be superior to other, conventional esterifications.

In a 2-l. flask were placed 387 g. (3 moles) of 1,3-dichloro-2-propanol, 50 g. of freshly fused sodium acetate, and 380 ml. (excess of 4 moles) of acetic anhydride. The mixture was slightly exothermic. After standing for one hour, the reaction mixture was refluxed for two days. The low boiling acetic acid and acetic anhydride mixture was distilled off at atmospheric pressure. The residue was distilled as follows:

Fraction	B.P., °C	Pressure, mm.	Capillary B.P., °C <u>at. press.</u>
1	86	14	---
2	50-70	1	198
3	53-71	1	202
4	74-87	1	229

Fractions 2 and 3 were combined to give 362.4 g. of product. The weight of the by-product, fraction 4, was 93.1 grams.

On redistillation of 1,3-dichloro-2-propyl acetate, a b.p. 198-198.5°C/748.5 mm. was observed.

D. 1,3-Dicyano-2-propyl Acetate:

Four attempts were made to react 1,3-dichloro-2-propyl acetate with sodium cyanide. Variations in relative concentrations, reaction media, product extraction procedures, and length of reaction time were studied.

From a total of 473.3 g. of ester processed, 22.6 g. of oily products were isolated. The combined oils were distilled in the presence of a few grams phenyl-beta-naphthylamine:

<u>Fraction</u>	<u>B.P., °C</u>	<u>Pressure, mm.</u>	<u>Remarks</u>
1	up to 79	2	Light yellow liquid with green fluorescence
2	78-90	2	Partially solid on cooling
3	91-97	1.5	" " " "
4	100-123	1	An orange oil
5	123-135	1	A dark oil
6	156-163	1	A dark oil
7	Solid residue		

The bulk of the distillate was to be found in the fractions 2,3,5 and 6. The residue was fractionally distilled through a 30 cm., glass-helix packed column.

<u>Fraction</u>	<u>B.P., °C</u>	<u>Pressure, mm.</u>	<u>Remarks</u>
I	59-60	26-27	A
II	75-78	14	B

A. a few drops of an orange liquid

B. main fraction, solidified in column and distillation head

In the course of this distillation, the column and distillation head rapidly clogged up when the main fraction suddenly crystallized. As a

result, the pressure built up and blew the system apart. The ensuing fumes had to be combated by dousing the apparatus with water.

It is believed that future attempts of this preparation could profitably utilize an electrically heated distillation column.

E. 1,3-Dibromobutane:

This method was a modification of the preparation originally proposed by Fargher and Perkin (79).

To a rapidly stirred dispersion of 186 g. (6 g.-atoms) of red phosphorus in 1 liter of benzene was added over a period of three hours 477 ml. (ca. 1440 g., a slight excess of 18 g.-atoms) of bromine. By cooling with a water bath, the reaction temperature was moderated. After completion of the addition, the reaction mixture was refluxed for three hours.

To the cooled solution of phosphorus tribromide thus prepared, were added 811.1 g. (9 moles) of 1,3-dihydroxybutane over a period of 1.25 hours with stirring. The mixture was stirred overnight and then refluxed for 2 hours.

After the benzene had been partially distilled off, the reaction mixture was washed in turn with water and sodium bicarbonate solution until neutral to litmus. The aqueous washes were extracted several times with benzene. The benzene washes were added to the product layer, checked for a neutral pH and dried over calcium chloride.

The benzene was distilled off at atmospheric pressure, leaving a residual product of 1096.0 g. (56.4% yield). This charge was distilled as follows:

<u>Fraction No.</u>	<u>B.P., °C</u>	<u>Pressure, mm.</u>	<u>Remarks</u>
I	60	28	discarded
	70	25	
II	71	28	Main Fraction
	76	31	
	70	19	
III	81	20	1022.0 g.
	112	22	

A tan residue, possibly of polymeric nature, remained.

While taking fraction II, a separate center weight was collected in the course of the distillation of this fraction. This special weight was labeled IIA.

The remaining fraction II was percolated through a 3 foot column packed with activated silica gel, which removed a colored contaminant.

<u>Properties</u>	<u>II A</u>	<u>II</u>
Capillary b.p.	172°/758 mm.	174°C/758 mm.
Z	38.8	38.6
n _D ²²	1.5050	1.5050
d ₂₅	1.7519 g./ml.	1.7718 g./ml.
Weight available	245.7 g.	739.9 g.

F. 1,3-Dicyanobutane:

To a 500 ml. three-necked flask, equipped with condenser, stirrer, and addition funnel, in which had been placed 67 g. (0.5 moles) of silver cyanide and 100 ml. of dry toluene, and which had been heated to reflux, was added 60 g. (0.25 moles) of 1,3-dibromobutane, dissolved in dry toluene, over a period of one and one-half hours. Reflux was maintained for 17 hours.

The solid was then filtered off, the filtrate was distilled. After removal of the toluene, a fraction with b.p. 59°C/12 mm. was isolated. This was considered recovered starting material.

A similar attempt, substituting sodium cyanide for silver cyanide and run in a water-methanol medium, showed evidence of reaction; however, exhaustive extraction of the product mixture with ether gave only a few grams of material boiling in the range of the starting material. The materials were unstable on exposure to air.

As had been noted generally in this group of experiments, prolonged exposure to heat tended to bring about extensive decomposition of the reaction product to form a black solid.

G. alpha-Methylglutaric Acid

In a 1-l. three-necked flask fitted with stirrer, addition funnel, and condenser, 27 g. (.5 moles) of commercial sodium methylate and 1 g. phenyl beta-naphthylamine were dissolved in 200 ml. of methanol. To this solution, 84.8 g. (0.53 moles) of diethylmalonate was added. After the solution had been refluxed for one-half hour, 51 g. (0.51 moles) of methyl methacrylate was added slowly. Reflux was continued for eleven hours. Then, a solution of 90 g. of potassium hydroxide in 250 ml. of water was added and reflux maintained for an additional three and one-half hours.

The condenser was then set down for distillation. The decarboxylation was carried out by adding 450 ml. of a hydrochloric acid solution (1:1) to the boiling solution at such a rate that the volume in the flask remained essentially constant while addition proceeded and low boiling solvent distilled out. After completion of the addition, the condenser was again set up for refluxing, and reflux continued for approximately twenty hours.

The aqueous solution remaining after this treatment was quite saturated with respect to sodium and potassium salts; consequently, organic material could be extracted with methanol. The solvent was evaporated from the extract. The residual oil was extracted with ether. The ether extract was preserved for final purification.

By a similar procedure, methyl cyanoacetate and methyl methacrylate were condensed together. The product was subjected to alkaline hydrolysis for fifteen hours. The decarboxylation step was carried out by acidifying the mixture with sulfuric acid and refluxing. The organic layer that formed was separated and preserved for final purification.

In a further run, the condensation of methyl cyanoacetate with methyl methacrylate was carried out in the presence of sodium methylate freshly prepared from sodium and absolute methanol with results that were comparable to all previous runs.

The products from these preparations were purified by repeatedly dissolving them in alkaline solutions, refluxing the solution, extracting with ether, liberating the acid from its salt with sulfuric acid, and extracting it with ether. These last ether extracts were evaporated. After several weeks the residues crystallized partially. The crystalline material could not be properly purified since separation of the oily portions was difficult.

H. 1-Methyl-1,3-dibromoglutaryl bromide:

In a 250 ml. three-necked flask fitted with a reflux condenser which was connected through a gas drying tube to a gas trap, a glass stirrer, and an addition funnel, were placed 39 g. (appr. 0.26 moles) of alpha-methylglutaric acid, 7 g. (0.22 moles) of red phosphorus, and 100 ml. of anhydrous benzene.

This mixture was rapidly stirred while 61 ml. (177 g., 1.1 moles) of bromine was added over a five hour period. This reaction was found to be highly exothermic.

The reaction mixture was refluxed for an additional eight hour period. A sufficient excess of bromine was added so that bromine vapor persisted for an appreciable length of time in the reflux condenser.

The excess bromine and the solvent were removed by evaporation. The residue was fractionally distilled through a 30 cm., glass-helix packed column.

Fraction	Boiling range, °C.	Pressure, mm.	
I	59-60	26-27	A
II	75-78	14 mm.	B

A. a few drops of an orange liquid

B. main fraction, solidified in column and distillation head

In the course of this distillation, the column and distillation head clogged up because the main fraction suddenly crystallized. The pressure build-up blew the system apart. The ensuing fumes had to be combated by dousing the apparatus with water.

X. Heptafluoropropylacrylamide

A. 1-Iodoperfluoropropane

1. Silver Perfluorobutyrate:

In one preparation, 117.7 g. (0.507 moles) of silver oxide in 250 ml. of benzene was heated over a period of one and one half hours with 214 g. (1 mole) of perfluorobutyric acid. An additional 50 ml. of benzene was added and reflux continued for an additional three and one half hours. In this period 9.3 ml. of water was collected in the water take-off tube.

The hot solution was filtered rapidly into 1250 ml. of textile spirits. The precipitate was collected from the cooled supernatant liquid. Weight of first crop 237.4 g. The mother liquor, on evaporation to dryness, afforded an additional 65.3 g. of product, bringing the total to 302.7 g. (94% of theory). M.p. of the first crop of crystals was 296-296.5°C (uncorr.)

Other preparations were run following the more conventional method of Hauptschein and Grosse (73). Yields were comparable; however the quality of the product was considered to be higher when prepared by the new method given above.

2. Iodoperfluoropropane:

Following the directions of Hauptschein and Grosse (73) closely, a mixture of 74.0 g. (0.24 moles) of powdered silver perfluorobutyrate and 64.4 g. powdered iodine were refluxed with stirring in an apparatus fitted with a Dry Ice condenser and connected to a Dry Ice-methanol trap. From time to time dry nitrogen was used to sweep the product into the Dry Ice-methanol trap. Whenever this was done, a more vigorous carbon dioxide evolution ensued. The reaction seemed to be complete in approximately seven hours.

Since some iodine had been swept into the trap containing the product, the following method was devised for purifying the product (which, it was noted, is liquid at Dry Ice temperatures and boils slightly above 40°C at ordinary pressures). A few crystals of sodium thiosulfate were introduced into the trap containing the product while the product was still quite cold. Then a few drops of water was added. As the product gradually warmed to the

melting temperature of water, the added water furnished enough moisture to permit the gradual interaction between iodine and sodium thiosulfate, at the same time keeping the material substantially anhydrous. As soon as the material had become colorless it was returned to the Dry Ice-methanol bath and cooled sufficiently to freeze the water. The clear product was then decanted and preserved in a sealed ampoule under nitrogen. The yield was 41.0 g. (60% of the theory). This product, on standing at room temperature and in daylight, rapidly takes on a pink coloration due to liberated iodine.

The following table will indicate the materials used and yields obtained in the preparation of further quantities of 1-iodoperfluoropropane.

Run No.	Wt. of Silver per- fluorobutyrate, g.	Wt. of Iodine, g.	Yield of 1-iodoper- fluoropropane, g.	% Yield
I-50	160.5	152.4	72.1	48.6
II-22	7.14	62.0	34.1	42
II-27A	80.2	68.8	43.1	50
II-27B	80.2	68.8	41.6	50
II-27C	80.2	68.8	53.0	70

The available 1-iodoperfluoropropane was treated in turn with sodium thiosulfate, manganese dioxide, and dried over potassium fluoride. The liquid was then distilled. The fraction with boiling point of 40.6 to 44.4°C at the prevailing atmospheric pressure was preserved as the desired 1-iodoperfluoropropane. The combined yield was 106.5 grams.

B. Heptafluoropropylamine

1. Hofmann Rearrangement:

An attempt to bring about the Hofmann rearrangement with 213 g. (1 mole) of perfluorobutyramide and 160 g. (1 mole) of bromine in the presence of 2 moles of freshly prepared sodium methylate, according to the procedure of Wallis and Lane (71), was unsuccessful.

2. Curtius Rearrangement

a. Heptafluorobutyrylhydrazide:

Treatment of 100% hydrazine hydrate with methyl perfluorobutyrate in the conventional manner afforded a 97% yield of heptafluorobutyrylhydrazide. m.p. 77.5-78°C (crystallized from water), after sublimation m.p. 78-78.5°C. Analysis of sublimate. Calc. for $C_4H_3F_7ON_2$: N, 12.3%; Found: 11.9%.

b. Rearrangement:

The procedure used was that described in Organic Reactions (72).

The product isolated from the reaction, recrystallized from dichloroethane, had a melting point of 166.5-167°C. Analysis: Found: C, 22.6; N, 6.8; H, 0.5%. Calculated for diheptafluorobutyrylhydrazide: C, 22.7; N, 6.6; H, 0.48%.

The hydrolysis of the product afforded hydrazine, identified by conversion to the dibenzoyl derivative. Thus the possibility of urea formation during the rearrangement was eliminated.

In any event, this method also did not afford the desired precursor of heptafluoropropylamine.

3. Ing-Manske Reaction:

Three attempts were made to prepare N-perfluoropropylphthalimide from phthalimide and 1-iodoperfluoropropane in the presence of potassium carbonate in a sealed bulb under a variety of temperature conditions. No N-alkylated product could be isolated in any of the attempts.

4. Gabriel Reaction:

The reaction of 1-iodoperfluoropropane with potassium phthalimide was attempted in a sealed bulb. No appreciable reaction was observed to take place and starting materials were recovered.

5. Delepine Reaction:

An unsuccessful attempt was made to prepare heptafluoropropylamine from 1-iodoperfluoropropane and hexamethylene tetramine by the method of Delepine.

XI. N-Alkyl-N-1,1-dihydroheptafluorobutylacrylamides and
N-Alkyl-N-1,1-dihydroheptafluorobutylmethacrylamides

A. N-Alkyl-heptafluorobutyramides:

The method used was essentially that described by Gilman and Jones (74).

To an ice-cooled solution of methyl perfluorobutyrate in ether was added gaseous ammonia or the appropriate amine. After the removal of the excess amine and the solvent, the residual amide could be crystallized or distilled depending upon the physical state of the amide at room temperature. The essential data is summarized in Table V.

TABLE V

Data for the Preparation of Perfluorobutyramides

Wt. of Methyl Perfluoro- butyrate, g.	Name of Amine Used	Wt. of Amine, g.	Wt. of Amide, g.	% Yield	B.P. of Product °C/ mm.
2532.1	ammonia	240	2246	95	
684	ammonia	63.3	600	93	
2160	methylamine	590	1910	89.8	167/756
2736	ethylamine	750	2665	92.5	168/759
2736	n-butylamine	1000	3120	96.6	192/766
2736	iso-butylamine	1059	3100	96.0	184/761
319.2	1,1-dihydrohepta- fluorobutylamine	298.5	353.8	63.6	169/756

B. N-Alkyl-1,1-dihydroheptafluorobutylamines:

The preparation of the amines by the lithium aluminum hydride reduction was carried out in two modifications. The older method was similar to that of Nystrom and Brown (75). The newer method does not involve the intermediate isolation of the amine acid sulfate. It liberates amine

directly from the reaction mixture in substantially better yields.

The preparation of 1,1-dihydroheptafluorobutylamine is a typical example of the older method, while the second preparation of N-ethyl-1,1-dihydroheptafluorobutylamine is representative of the newer method.

1. 1,1-Dihydroheptafluorobutylamine:

In a 12-l. three-necked flask equipped with a mercury sealed stirrer, dropping funnel, gas inlet tube, and reflux condenser which was protected from atmospheric moisture by a calcium chloride tube, was placed 4 liters of absolute ether.

The whole apparatus was placed behind a protective shield and on top of disposable aluminum foil. Any lithium aluminum hydride which might fall on the aluminum foil was to be covered with sand and at the end of reaction the aluminum was to be destroyed by burning. Into the ether was slowly added 123 g. (3.2 moles) of lithium aluminum hydride. All the precautions for handling the hydride were maintained throughout the preparation. Nitrogen gas was then passed into the system. The mixture was stirred for two additional hours after the hydride had been added. A slight opaque solution resulted.

A solution of 532.5 g. (2.5 moles) of perfluorobutyramide in 1000 ml. of anhydrous ether was added dropwise. Evolution of gas was observed after each drop of amide solution came in contact with hydride solution. The flask was placed in an ice-bath to moderate the heat of the reaction. It took three hours to add the amide solution. A somewhat white translucent solution resulted. An additional liter of ether was added to the mixture to make up for the ether lost due to entrainment.

The mixture was stirred overnight. The nitrogen gas was continually passed through the system during the night. It was then heated to reflux for four hours. An ice-salt bath was placed around the flask and the contents was then cooled to below 5°C.

The nitrogen flow was increased to 5-6 cu. ft./hour. Then 200 ml. of water was added in a very slow dropwise manner.* A vigorous evolution

* In subsequent preparations, ethyl acetate was used, instead of water, to decompose the excess lithium aluminum hydride. This was found to be much less vigorous and much safer.

of gas occurred following each drop of water. Refluxing of the solution was maintained at a minimum by controlling the rate of water addition. Immediately after all the water had been added, an ice-cold solution containing 780 ml. of concentrated sulfuric acid and 1800 g. of ice was added slowly with continued cooling of the reaction flask. The semi-solid slurry which resulted was stirred for an additional hour. The solid which separated consisted of the 1,1-dihydroheptafluorobutylamine acid sulfate. This was collected on a filter and washed with ether and finally air dried. The dried amine salt was ground to a fine powder and placed in a 3-l. three-necked flask, equipped with a stirrer, dropping funnel, and reflux condenser. To the solid was added slowly 2-l. of 50% sodium hydroxide solution. An ice-bath was placed around the flask to moderate the heat of neutralization. The mixture was stirred for an additional hour after all of the sodium hydroxide solution had been added.

The alkaline mixture was then distilled through a 50 cm. glass helix-packed, silver-lined, vacuum-jacketed column with total condensation, partial take-off head. The 1,1-dihydroheptafluorobutylamine was collected at 65-68°C. It was a water white liquid with a refractive index, n_D^{21} 1.300. (Lit.(77). b.p. 68°, n_D^{20} 1.298.) A yield of 263 grams or 52.8% of the theoretical was obtained.

Redistillation of the product gave b.p. 63°C/746 mm.

This procedure was carried out several times to obtain sufficient material for subsequent preparations.

2. N-Alkyl-1,1-dihydroheptafluorobutylamines:

The general procedure for the reduction of N-alkylperfluorobutyramides with lithium aluminum hydride has been given above.

In Table VI the pertinent data for more of these preparations are summarized.

Column A states the alkyl substituent under consideration.

Column B, weight and number of moles of lithium aluminum hydride used.

Column C, the quantity of ether used to dissolve the reducing agent initially.

Column D, weight and number of moles of N-alkyl-heptafluorobutyramide used, dissolved in 1 liter of ether.

Column E, addition time of amide solution.

Column F, time the reaction was maintained at room temperature.

Column G, approximate volume of ethyl acetate used to react with the excess of lithium aluminum hydride.

Column H, the volume of concentrated sulfuric acid diluted with the volume of ice stated in Column I, which was added to precipitate the final product.

In each of these preparations, the solid which had precipitated from solution on addition of acid was filtered off and air dried as the product.

TABLE VI

Data for the Preparation of

N-Alkyl-1,1-dihydroheptafluorobutylamine bisulfates

A	B	C	D	E	F	G	H	I
Methyl	100 g. 2.65 moles	1-l.	726.4 g. 3.2 moles	1 hr.	16 hr.	500 ml.	560 ml.	1500 ml.
Ethyl	"	3	725 g. 3 moles	3	72	"	"	"
n-Butyl	"	1	760 g. 2.8 moles	2	22	"	"	"
iso-Butyl	"	1	864 g. 3.2 moles in 1.5-l. ether	3.75	18	"	"	"
	"	1	864. g. 3.2 moles in 1-l. ether	2	4 in water at 50°	140	1000	1000
1,1-dihydro- heptafluoro- butyl*	39.6 1 mole	1	316 g. 0.8 moles	.75	1	200	225	600

* In the case of the reduction of N-(1,1-dihydroheptafluorobutyl) heptafluorobutyramide, 145 g. of unreacted starting material was recovered from the ether solution after the reaction had apparently gone to completion.

The general method for the liberation of amine from its bisulfate salt has been indicated in the example above. In Table VII, the pertinent information for these preparations is given:

Column A gives the alkyl group under consideration,
 Column B, weight of bisulfate salt,
 Column C, volume of water in which salt was dispersed,
 Column D, volume of 50% sodium hydroxide used,
 Column E, boiling range of product, °C,
 Column F, weight of amine isolated, g.
 Column G, boiling point of product, °C/mm. Hg.

TABLE VII

Data for the Preparation of
 N-Alkyl-1,1-dihydroheptafluorobutylamines

A	B	C	D	E	F	G
Methyl	930 g.	500 ml.	1560 ml.	71-74°C 765 mm.	121.2 g.	84 °C 756 mm.
Ethyl	1050	500	2000	80-95	136.5	96-98 75
n-Butyl	1000	1000	1100	81-97	192	133 741
iso- Butyl	792	None	1500	89-100	67.4	130 765

3. N-Ethyl-1,1-dihydroheptafluorobutylamine

In a 5-l. three-necked flask, fitted with addition funnel, gas-inlet

tube, mechanical stirrer, and a long reflux condenser which was connected to a drying tube, under a nitrogen atmosphere, 60 g. (1.6 moles) of lithium aluminum hydride was dissolved in 600 ml. of anhydrous ether. To this solution 435 g. (2 moles) of N-ethylheptafluorobutyramide in 500 ml. of anhydrous ether was added over a three hour period while the flask was being cooled in ice and a nitrogen stream passed through the whole system.

After allowing the reaction mixture to warm to room temperature overnight, the mixture was warmed cautiously with water at approximately 60°C for 5 hours.

The decomposition of the excess lithium aluminum hydride was carried out by the cautious addition of approximately 150 ml. of anhydrous ethyl acetate, followed by the addition of 500 ml. of water. The ether solution was separated. The product was divided by distillation into an ether fraction, b.p. 33-59°C at atmospheric pressure, a product fraction b.p. 59-120°C, and a higher boiling residue. From this latter and other high boiling residues obtained during the distillations, a total of 128 g. of unreacted N-ethylheptafluorobutyramide (b.p. 167-168°C/759 mm.) was recovered. From the intermediate fraction, 92.5 g. of product was obtained by distillation. Yield: 30% based on utilized material.

The aqueous phase and precipitates were worked up by steam distillation and ether extraction. However only trivial amounts of amine could be isolated.

By similar procedures, one run of the N-iso-butylamine was carried out as well as the successful preparation of di(1,1-dihydroheptafluorobutyl) - amine.

In the latter case, 41.9 g. (0.1 moles) of the corresponding amide was reduced with 7 g. (0.2 moles) of lithium aluminum hydride. The final product had a boiling range of 134 to 140°C/752 mm., yield was 34.5 g., 90% of theory.

B. N-Alkyl-N-1,1-dihydroheptafluorobutylacrylamides

1. N-1,1-Dihydroheptafluorobutylacrylamide:

In a 3-l. three-necked flask, equipped with a mercury-sealed stirrer, dropping funnel, and reflux condenser was placed 263 g. (1.32 moles) of 1,1-dihydroheptafluorobutylamine and 1250 ml. of anhydrous ether. A solution containing 58.8 g. (0.66 moles) of redistilled acrylyl chloride

dissolved in 250 ml. of anhydrous ether was added slowly to the amine solution. At each drop vigorous refluxing of the ether took place with subsequent deposition of solid amine hydrochloride.

The mixture was stirred for an additional hour. No amine odor or acrylyl chloride odor persisted in the mixture. This was filtered and the amine hydrochloride, which was collected on the filter, was washed three times with 50 ml. portions of anhydrous ether. The air-dried 1,1-dihydroheptafluorobutylamine hydrochloride weighed 146 g. representing a 94.5% reaction. The hydrochloride melted with sublimation at 220-230°C

The ethereal filtrates were combined and flash vacuum distilled at room temperature. A white solid remained which weighed 163 g. This represented a yield of 97.5%. The crude N-(1,1-dihydroheptafluorobutyl)-acrylamide melted at 56-57°C.

Solubility studies of the acrylamide were carried out in order to determine the best solvent for recrystallization. This study was based on attempting to dissolve 0.3 g. of the amide in 10 ml. of solvent.

Solubility was observed at room temperature and at the boiling point of the solvent. If the fluorobutylacrylamide was insoluble in the cold solvent but soluble in the hot solvent then this solvent was considered as being suitable for use in the recrystallization. Table VIII gives the solvents used and the results.

TABLE VIII

Recrystallization Studies with

N-(1,1-Dihydroheptafluorobutyl)-acrylamide

<u>Solvent</u>	<u>Remarks</u>
1. Ethyl Acetate	Completely soluble at room temperature and at ice temperatures.
2. 1-Butanol	Completely soluble at room temperature.
3. 50% Methanol Solution (50% water-50% methanol)	Completely soluble at room temperature, slight haze when cooled to 0°C.
4. 25% Methanol Solution (75% water-25% methanol)	Soluble at room temperature, but crystallized out at ice temperatures. Crystals not defined.
5. 50% Acetone Solution (50% water-50% acetone)	Soluble at room temperature.
6. 25% Acetone Solution (25% acetone-75% water)	Soluble at room temperature; slight haze at ice temperature.
7. Benzene	Soluble at room temperatures.
8. 50% Petroleum Ether and 50% Benzene	Insoluble at room temperature. Soluble at elevated temperature. Very little of the material crystallized on cooling.
9. Petroleum Ether (30°C- 60°C range)	Insoluble in cold. Soluble in the hot and crystallized on cooling. Approximately 80% is recovered recrystallized material. M.P., very sharp, 57.4 - 57.6°C.

On the basis of Table VIII, it was decided to recrystallize the fluorobutylacrylamide from petroleum ether.

The 260 g. of N-1,1-dihydroheptafluorobutylacrylamide was suspended in 8500 ml. of boiling petroleum ether. A clear homogenous solution resulted and on cooling in an ice bath the amide crystallized out in beautiful fine, white needles. There was obtained 195 g. or 75% recovery of the amide; melting point 57.4-57.6°C.

The acrylamide gave positive bromine and potassium permanganate tests.

A two gram sample of the above recrystallized acrylamide was taken for analysis and was twice recrystallized from petroleum ether. A melting point of 57.5-57.6°C was obtained. The material readily sublimed at 35°C and 2 mm. pressure. Analysis. Calc'd. for $C_7H_4ONF_7$: C, 33.21; H, 2.39; N, 5.54. Found: C, 33.40; H, 2.50; N, 5.60.

2. N-Alkyl-N-1,1-dihydroheptafluorobutylacrylamide:

In general the acrylamides were all prepared as follows: In a 500 ml. three-necked flask fitted with condenser, gas inlet tube, stirrer and addition funnel, approximately 0.25 moles of the free amine was dissolved in 50 ml. of anhydrous ether and 25.1 g. (0.25 moles) of triethylamine was added.

The addition of an equivalent amount of freshly distilled acrylyl chloride, free of inhibitor, in 50 ml. of anhydrous ether took place under a nitrogen atmosphere. The reaction mixture was rapidly filtered free of triethylammonium chloride, hydroquinone was added to the filtrate, and the filtrate was thereupon fractionally distilled.

The pertinent data for a typical series of preparations is given in Table IX.

Column A states the alkyl group under consideration

Column B, weight used and number of moles of amine

Column C, weight of acrylyl chloride and number of moles of acrylyl chloride used

Column D, addition time

Column E, boiling range of product

Column F, weight of product

Column G, percentage yield

Column H, boiling point of product, °C/mm. Hg.

TABLE IX

Data for the Preparation of

N-Alkyl-N-1,1-dihydroheptafluorobutylacrylamides

A	B	C	D	E	F	G	H
Methyl	53.2 g. 0.25 moles	22.6 g. 0.25 moles	30 min.	95°C/21 mm. to 101°C/33mm.	27.2 g.	41%	77°C 8 mm.
Ethyl	50.5 g. 0.22 moles	22.6 g. 0.25 moles	90	94°C 14 mm.	38.1	61	94 14
n-Butyl	64 g. .25 moles	22.6 g. 0.25 moles	60	111°C 14 mm.	42.3	53	111 14
iso- Butyl	49 g. 0.19 moles	18 g. 0.2 moles	90	110-113°C 18 mm.	30.5	52	107 15

The preparation of N,N-di(1,1-dihydroheptafluorobutyl)-acrylamide was attempted. The reaction involved 16 g. (0.042 moles) of di(1,1-dihydroheptafluorobutyl) amine in 25 ml. of anhydrous ether and 10 g. (0.1 moles) of triethylamine with a solution of 3.82 g. (0.042 moles) of acrylyl chloride in 25 ml. of anhydrous ether.

After the removal of ether and the excess of triethylamine, the residue was fractionally distilled into three fractions:

<u>Fraction No.</u>	<u>B.P. range</u>	<u>Refractive Index</u>
A-1	32-40°C/ 15 mm.	n_D^{20} 1.3532
A-2	74-85°C/ 14 mm.	1.3431
A-3	67-82°C/ 14 mm.	1.3472

Redistillation resulted in one large fraction of boiling point 26°C at 20 mm. and another fraction with a boiling point of 58°C at 20 mm.. The latter fraction consisted of two phases. The total weight of the two fractions was 1.5 grams. In view of the low yield, and the obvious question of the nature of the two phases, this preparation would have to be repeated before an adequate identification could be possible.

3. N-Alkyl-N-1,1-dihydroheptafluorobutylmethacrylamides:

The method of preparation of the methacrylamides was essentially the same as that employed for the preparation of the acrylamides except that methacrylyl chloride, free of inhibitor, was substituted for acrylyl chloride in the preparation.

In Table X the pertinent data for these preparation are given.

Column A, states the alkyl group under consideration

Column B, weight used and number of moles of amine

Column C, weight and number of moles of methacrylyl chloride

Column D, addition time, hours.

Column E, boiling range of product, °C/mm. Hg.

Column F, weight of product, g.

Column G, percentage yield

TABLE X

Data for the Preparation of

N-Alkyl-N-1,1-dihydroheptafluorobutylmethacrylamides

A	B	C	D	E	F	G
Methyl	21.3 g. 0.1 moles	10.5 g. 0.1 moles	0.5	81.5-82°C hrs. at 8 mm.	23.9	85%
Ethyl	22.5 g. 0.1 moles	10.5 g. 0.1 moles	0.6	102-109 29	13.1	46.5
n-Butyl	25.5 g. 0.1 moles	10.5 g. 0.1 moles	0.3	65-114 19	18.6	60.2
iso-Butyl	25.5 g. 0.1 moles	10.5 g. 0.1 moles	0.6	76-95 5	11.2	36
1,1-Dihydrohepta- fluorobutyl	16 g. 0.042 moles	44 g. 0.042 moles	0.5	41-89 24	5.3 (a)	28.7

(a) This product was a combination of three fractions

A.	41-48°C/24 mm.	n_D^{20}	1.3005
B.	84-89°C/24 mm.		1.4360
C.	89°C/24 mm.		1.444

The quantities involved were considered too small for proper identification of the fraction.

XII. Polymerization Studies

A. Preparation of Monomers

The two available methods for removing inhibitor from monomers preliminary to polymerization were distillation and washing with dilute sodium hydroxide solution.

Those monomers which were distilled were fractionated through a 30 cm. column packed with 1/8" glass helices and equipped with a total reflux, partial takeoff head. The higher boiling monomers were fractionated under vacuum.

Some monomers were washed with several portions of 2% sodium hydroxide solution. One wash after the first colorless wash was used. The alkali washes were followed by three washes with water and a last wash with saturated sodium chloride solution for preliminary drying. The monomers were then dried over anhydrous magnesium sulfate.

The following monomers were investigated. In each case the method of purification is specified.

Ethyl Acrylate	Distilled, b.p. 98-9°C
Acrylonitrile	Distilled, b.p. 76-8°C
n-Butyl Acrylate	Washed
2-Methoxyethyl Acrylate	Distilled, b.p. 65°C/20 mm.
2-Ethylhexoxyethyl Methacrylate	Distilled, b.p. 149-152°C/18 mm. then washed
2-Methoxyethyl Methacrylate	Distilled, b.p. 72°C/16 mm.
n-Butyl Methacrylate	Washed
Methacrylonitrile	Distilled, b.p. 89-90°C
n-Butoxyethyl Acrylate	Distilled, b.p. 92°C/12 mm.
2-Ethylhexoxyethyl Acrylate	Distilled, b.p. 137-8°C/13 mm.

B. Emulsion Polymerizations:

The first polymerizations, for comparison purposes, used the monomer compositions of American Monomer's Acrylon EA-5 and EA-10, i.e. ethyl acrylate with 5% and 10% acrylonitrile respectively. The recipe used consisted of 30 ml. of water, 1 g. of Dupanol ME, 0.5 g. of potassium persulfate, and 30 g. of total monomers. The mixtures were placed in 4 oz. bottles and fastened to a shaker immersed in a thermostated water bath. The bath was maintained at $79^{\circ}\text{C} + 1.5^{\circ}$. After 15 hours, the bottles were removed. A large lump of rubber in addition to latex was found in each bottle. It was concluded that the ratio of monomer to aqueous phase and the ratio of catalyst to monomer were too high.

Another set of polymerizations of EA-5 and EA-10 was run using the following recipe: 45 ml. of water, 0.75 g. of Dupanol ME, 0.4 g. of potassium persulfate, and 25 g. of total monomers. Other conditions were the same as in the first experiment. On removal from the bath, a small plug of rubber was attached to the cap of the bottle, but on standing a short time, both EA-5 emulsions agglomerated into lumps composed of small ellipsoidal nodules. Neither of the two EA-10 latices prepared behaved in this way.

A third modification of the recipe was made. Mixtures of 45 ml. of water, 1 g. of Dupanol ME, and 0.15 g. of potassium persulfate with 25 g. of total monomers were polymerized. A slight deposit was found in the bottle caps. The emulsions had a blue cast. Neither the EA-5 nor the EA-10 emulsions began to coagulate on removal from the bath.

With a recipe which was successful with EA-5 and EA-10, a more extensive series of polymerizations was carried out. In addition to compositions corresponding to the Acrylon rubbers BA-5, BA-12, and BA-20, the following monomers were used, each with 10%, 25%, and 50% acrylonitrile: n-butyl methacrylate, 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, and 2-ethylhexoxyethyl methacrylate. The bottles were flushed with nitrogen before being placed in the bath. Unfortunately, though the recipe proved adequate for all the Acrylon rubbers, this did not guarantee a good emulsion with other formulations. All three polymers containing 2-methoxyethyl acrylate precipitated as solid lumps in aqueous phases which were clear liquids. As might have been expected, all the polymers containing 50% acrylonitrile were hard and brittle. In addition, these polymers were obtained as solid lumps in clear aqueous phases. With the above exceptions, good latices were obtained.

The precipitation of a latex in the form of a fine crumb which could be adequately washed was considered desirable. Experiments in which latices were precipitated by pouring into aluminum sulfate solutions with hand stirring resulted in lumps of rubber which could not be washed adequately.

The same result was obtained with alum solutions ranging from 0.25% to 2% and containing from 0 to 35% methanol.

It was sometimes possible to precipitate an emulsion as easily broken up lumps by diluting the contents of a bottle with 100 ml. of water and 50 ml. of methanol, and adding 50 ml. of 1% aluminum sulfate solution with hand stirring. However, the desired result was not always obtained.

A series of 32 latices was prepared. To each bottle was added 25 ml. of solution containing 1 g. of Dupanol ME. The monomers (total 25 grams) were then added, followed by 25 ml. of a solution containing 0.15 g. of potassium persulfate. The bottles were flushed with nitrogen and shaken in the water bath at 79°C during 15 hours. In Table XI, the following abbreviations are used: acrylonitrile-AN, n-butyl acrylate-BA, 2-methoxyethyl acrylate-MEA, 2-methoxyethyl methacrylate MEMA, ethyl acrylate-EA, n-butyl methacrylate-BMA, methacrylonitrile-MAN, n-butoxyethyl acrylate-BEA, 2-ethylhexoxyethyl acrylate-EHEA, acrylamide-AA.

TABLE XI

Experimental Polymer Compositions

<u>Bottle</u>	<u>Composition</u>				
1	20	% AN	40	% BA	40 % MEA
2	20	AN	60	BA	20 MEA
3	20	AN	72	BA	8 MEA
4	20	AN	40	BA	40 MEMA
5	20	AN	60	BA	20 MEMA
6	20	AN	72	BA	8 MEMA
7	25	AN	37.5	BA	37.5 MEA
8	20	AN	40	EA	40 MEA
9	15	AN	42.5	BEA	42.5 MEA
10	10	MAN	90	EA	----
11	5	MAN	95	EA	----
12	12	AN	44	BA	44 BMA
13	12	AN	66	BA	22 BMA
14	12	AN	79.2	BA	8.8 BMA
15	5	MAN	95	BMA	----
16	10	MAN	90	BMA	----
17	12	AN	44	BA	44 EHEA
18	12	AN	22	BA	22 EHEA
19	12	AN	79.2	BA	8.8 EHEA

TABLE XI (cont.)

	10	% MAN	90	% MEA	----	%
20						
21	33	AN	67	BEA	----	
22	20	AN	80	BEA	----	
23	10	AN	90	BEA	----	
24	20	AN	40	BEA	40	BA
25	20	AN	20	BEA	60	BA
26	20	AN	8	BEA	72	BA
27	25	AN	37.5	BA	37.5	BA
28	20	AN	40	BEA	40	EA
29	10	AN	45	BEA	45	EA
30	10	AN	22.5	BEA	67.5	EA
31	10	AN	10	BEA	80	EA
32	20	MAN	80	BEA	----	

Of the above 32 preparations, nos. 8,9,20 and 21 formed single large lumps of rubber. Nos. 2,3,4,5,6,7,10,11,16,27,28,29,31 contained lumps of varying size with an appreciable amount of rubber in the form of latex.

The problem of avoiding the formation of a single tenacious lump of rubber on coagulation was not solved. When some lumps which had been washed as thoroughly as possible and allowed to dry were cut open, they were wet inside though the outside shell was thoroughly dry. In some cases uncoagulated latex was also present.

In the hope of improving the emulsion and the ease of coagulation, five emulsions were prepared using essentially the recipe described in reference (80).

TABLE XII

Experimental Polymer Compositions

<u>Bottle</u>	<u>Compositions</u>		
33	20 % AN	45 % EA	35 % MEA
34	10 AN	90 EA	----
35	5 AN	90 EA	5 AA
36	10 AA	45 EA	45 MEA
37	15 AN	42.5 EA	42.5 MEA

Each bottle contained 25 ml. of an aqueous solution of 0.4 g. of Tergitol Penetrant 4 and 0.266 g. of Triton X-200, and 25 ml. of a solution containing 0.15 g. of potassium persulfate. The total monomers per bottle was again 25 grams.

The rubber in bottles 33, 36, and 37 was in the form of single large lumps. A small amount of emulsion was present in #33. An inspection of all the results indicated that the poorest results were obtained with monomers having ether linkages, with the degree of trouble increasing with decreasing molecular weight. With a sizable percentage of 2-methoxyethyl acrylate, the rubber was almost invariably present in the form of a single large lump.

It was found possible using emulsions nos. 34 and 35 to improve prepipitation by following the procedure described in the above mentioned publication. Pouring the emulsion into 150 ml. of warm saturated sodium chloride solution with rapid stirring produced a very finely divided crumb which could be filtered by gravity and washed. On the filter this formed a solid sheet. After removing most of the water on a Büchner funnel, it was necessary to slice the lump of rubber to dry it effectively.

The decision was made to investigate bulk polymerization for several reasons. Though good emulsions could be obtained with the Acrylon rubber types, the introduction of polar groups such as ether linkages would have necessitated the development of a new recipe. Since it was intended to investigate a wide variety of monomers, such a program was not attractive. In addition, the processing of the emulsions seemed to involve an inordinate

amount of handling. Also the use of more water soluble monomers, for example acrylamide, could produce misleading results since some monomer might polymerize in solution in the aqueous phase.

C. Bulk Polymerization:

The feasibility of bulk polymerization was tested by running four compositions corresponding to Acrylon rubbers in sealed test tubes. Two sizes of tubes were used, the smaller containing 10 g. of monomer and the larger, 25 grams. The catalyst was 0.1% of benzoyl peroxide. The tubes were shaken in an agitated water bath at 68-70°C for 87 hours. The polymers were pale yellow, transparent materials.

Since test tubes were inadequate for the polymerization of large amounts, the use of aluminum foil bags was investigated. Two attempts made it apparent that the bags were too fragile and leaked too much for consistent results. Consequently, 8 oz. cans were selected as promising containers, which could hold an amount of monomer corresponding to the size of sample needed.

The contents of six cans polymerized satisfactorily in a hot air oven. Can no. 46 bulged somewhat at the top but did not lose any appreciable weight.

Can no. 49 blew open completely. Water leaked into can, no. 47, probably because vapors had been forced out during the exothermic phase of the reaction with a consequent reduction in pressure on cooling.

Some time was required to strip the can from the lump of rubber but this step appeared to be less time-consuming than the processing of an emulsion. The odor of the rubbers produced indicated that some unreacted monomer was present.

Apparently, a small percentage of acrylamide greatly increased the violence of the polymerization. Though heat transfer was undoubtedly more effective in the water bath, the possibility of water entering the can would have to be counted a disadvantage.

Bulk polymerizations were finally carried out as follows:

Mixtures of monomers were polymerized in 8 oz. cans. There was placed in each can a total of 200 g. of monomers containing 0.01% of a peroxide catalyst. The cans were flushed with nitrogen and closed with a screw cap.

In most cases, benzoyl peroxide was used. Since some of the polymerizations in which acrylamide was involved were rather violent, lauroyl peroxide was used to effect polymerization at a lower temperature.

Polymerizations with lauroyl peroxide as catalyst were started at 45°C, while those using benzoyl peroxide were started at 50-60°C. After the mixtures had set, the temperature in the oven was raised to 80°C and finally to 100°C. Ultimately, the cans were stripped from the rubber.

Even after prolonged heating at 100°C, the copolymers contained some residual monomer. To reduce or eliminate the residual monomer, the polymers were milled with rollers which were cooled by cold water. Because of the resilience of the rubber, it was not possible to produce smooth sheets. A sample of each rubber, therefore, was molded into a 2" x 3" sheet on a Carver press to provide a specimen in the proper physical form for weight loss and solvent resistance tests. The results of these tests are given in Table IV.

The blank spaces in Table IV for per cent. weight gain and volume increase in iso-octane--toluene solutions are a consequence of the deterioration of some samples in these solvents. The specimens were attached to pieces of wire. These wire handles were used to hang the rubber samples from the balance hook and to suspend them in the solvent mixture. Those samples for which figures are not given softened to such an extent that they slid off the wires and settled at the bottom of the test bottle as gummy masses which could not be handled properly.

A series of twenty-three copolymers was prepared too late for testing for heat and solvent resistance. The data for these, consequently, are not included in Table IV. The method of preparation of these copolymers was the same as for those previously described. The polymers were terpolymers using combinations of butyl acrylate, ethyl acrylate, acrylamide, and acrylonitrile with vinyl butyl ether and with vinyl chloroethyl ether.

Two 5 gram samples of trifluoroethyl acrylate copolymers containing 5% and 12% respectively of acrylonitrile were prepared under a nitrogen atmosphere in sealed test tubes. The polymerization was catalyzed by 0.01% of benzoyl peroxide.

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